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SYMPOSIUM ON INTERMOLECULAR ACTION¹

INTRODUCTION TO THE SYMPOSIUM²

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. The Third Annual Symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society is the second in the field of physical chemistry, as the Second Annual Symposium was devoted to inorganic chemistry. The first symposium discussed molecular structure, or the character of molecules. The present symposium discusses the behavior of molecules, which is, of course, determined by their character, although in our present state of knowledge it is often impossible to predict behavior from character or even to relate a particular behavior to any specific characteristic.

There is little, if any, chemistry not included under the two titles "Molecular Structure" and "Intermolecular Action". It was therefore necessary to restrict the field of this symposium much more than the title indicates. It seemed logical to discuss first the behavior of a normal molecular society rather than molecules excited enough to undergo deep-seated chemical changes. Therefore kinetics were excluded by the committee, and it has been tacitly assumed by all the contributors that any consideration of chemical equilibrium should emphasize its change as the medium changes rather than its absolute value in any one medium. If a group of molecules in the ground state (electronic) may be likened to an agricultural society,

¹ This Symposium on Intermolecular Action was held, as the Third Annual Symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society, at Brown University, Providence, Rhode Island, on December 27 to 29, 1938. The papers presented at the symposium were classified for discussion into five groups: Part I, Gases and Pure Liquids—J. C. Slater presiding; Part II, Non-polar Mixtures—H. Eyring presiding; Part III, Highly Polar Mixtures—J. G. Kirkwood presiding; Part IV, Polar Mixtures—N. Bjerrum presiding; Part V, Ionic Solutions—L. P. Hammett presiding. These papers follow the introduction in order, in this issue and in the February issue.

The arrangements for the symposium were made by a committee consisting of G. Scatchard, *Chairman*, E. J. Cohn, F. Daniels, H. Eyring, J. H. Hildebrand, L. S. Kassel, C. A. Kraus, V. K. LaMer, P. B. Leighton, and S. C. Lind.

² Contribution No. 412 from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology.

we are to discuss pastoral communities. We have not excluded the nomadic molecular life as manifested in diffusion, viscosity, and conductance, but we have limited our field further by ruling out the very highly organized molecular groupings of the solid state.

There is also a historical reason for this choice of subject. If physical chemistry can be said to have begun at any specified date, that date is February, 1887, when the *Zeitschrift für physikalische Chemie* was founded. The need for this journal arose from the great amount of work then being done on solutions, and such work has ever since filled a large part of this and similar journals. Even in the decade before 1887 the two subjects which seem to have thrilled the imagination of the inorganic chemist most were electrolysis and the liquefaction of gases.

No symposium can be justified either by logic or by history. The justification for this symposium must rest on the belief that the subject of "Intermolecular Action" is live enough in America today to afford a discussion which will stimulate, clarify, and point the way for future work. Substantial evidence of this life and interest is the new laboratory at Brown University, which will be dedicated on December 27th and which is already busy with work largely in this field.

The whole organization of this symposium has been planned to promote discussion. Those speakers were invited who were expected to provoke discussion, and they were asked to present new work rather than reviews. Unfortunately this procedure has eliminated some contributors from whom we should like to hear but who have no work in this field maturing in December, 1938. The number of papers has been restricted and preprints have been prepared, so that as much as possible of the time of the meetings may be devoted to discussion. The quality of the papers so obtained has exceeded our highest expectations, but we do not delude ourselves into taking credit for their quality, because we know that each of these papers would have been published somewhere if there had been no symposium. We do congratulate ourselves, however, that we have collected here the basis for a good discussion.

The method of selecting papers has made it impossible to attempt to cover the field evenly or thoroughly, for the committee had no way of knowing that part of the field to which many of the speakers would contribute. Yet the papers group themselves with very little stretching into five nearly equal parts covering the six subfields in which we expected contributions. The groups have been arranged in the order of increasing complexity of the intermolecular action with one exception,—slightly polar mixtures have been placed after both non-polar mixtures and highly polar mixtures. The reason for this order is that it is simpler to study two coexistent actions by considering first the case in which one exists alone, second the case in which the other predominates, and last the case in which the two are about equally important.

I shall make no attempt to review the large field of "Intermolecular Action" or to show its importance, but I cannot pass over the opportunity of gaining an insight into the present state of this branch of science and its rate of development by examining the distribution of papers, comparing it with the probable distribution if such a symposium had been held at some time in the past, and speculating a bit as to the reasons for the change. We must remember, of course, that a score of papers is not enough to eliminate the effect of requiring papers on a certain date and requesting that they be provocative of discussion, and I merely note in passing the improvement in precision both of measurements and of thinking which has taken place in the last few years. To me three developments are outstanding: The first is that the theorists are no longer confining their attention to the crystal lattice or to very dilute gases or solutions, but now offer us studies of liquids and concentrated solutions from three or four points of view. The second is that the Debye theory of interionic action appears to be no longer a question for discussion but is now taken for granted in the consideration of the more complicated effects of changing medium and of the detailed structure of the ions. The third, and perhaps the most important, is the growing recognition of the inherent unity of the subject "Intermolecular Action."

NOTE ON THE YEAR'S PROGRESS IN THE PRECISE MEASUREMENT OF THE EFFECTS OF INTERMOLECULAR POTENTIAL IN GASES^{1,2}

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Received October 12, 1938

INTRODUCTION

Some years ago (6) the attempt was made to measure the change of the enthalpy, or the thermodynamic potential, with pressure at various constant temperatures for low pressures. The impulse prompting the effort originated in the attempt to obtain exact information about the properties of gases and gas mixtures at low pressure by extrapolation from the available pressure, volume, temperature data, Joule Thomson numbers, and expansion coefficients. The preference for low pressure data is, of course, due to the interesting inferences which may be drawn as to the intermolecular potential through the application of statistical mechanics theory. Specifically, statistical mechanics establishes the fact that at low pressures (strictly zero pressure) the equation of state of gases may be written

$$p = \frac{RT}{V - B_0} \quad (1)$$

where B_0 is a function of the temperature³ and the intermolecular potential.

For identical particles of the non-polar type, whose intermolecular po-

¹ Presented at the Symposium on Intermolecular Action, held at Brown University, Providence, Rhode Island, December 27-29, 1938, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society.

² Contribution No. 409 from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology.

³ One of us has come to prefer this form of the equation rather than that more commonly encountered

$$pv = RT \left(1 + \frac{B_0}{v} \right)$$

The preference is based principally on the fact that in practice data are more readily correlated by equation 1. At low pressures the differences in form are of course insignificant.

tential, W , is spherically symmetrical (s states) the classical expression (high temperatures) is simple, *viz.*:

$$\begin{aligned} B_0 &= -\frac{2\pi N}{3kT} \int_0^\infty r^3 \frac{\delta W}{\delta r} \exp. \left(-\frac{W}{kT} \right) dr \\ &= 2\pi N \int_0^\infty \left[1 - \exp. \left(\frac{W}{kT} \right) \right] r^2 dr \end{aligned} \quad (2)$$

where r is the distance of separation of particle pairs.

It would be desirable to invert (9) this Laplace type integral equation and compute $W = f(r)$ directly, but it is easily shown that no results of value would result unless very exact values (1 in 1000) of B_0 at a series of temperatures were available. It is likely, however, that the methods employed to date, of using plausible and tractable forms for W and comparing the computed results from formula 2 (or its more general prototype) with the observed B_0 values, will lead ultimately to a sufficiently detailed knowledge of the intermolecular potential.

Equation 2, restricted to the case where the classical theory applies, must be replaced by a more general expression at lower temperatures where quantized collisions occur ($W > kT$) or where polar molecules are involved. Present quantum theory provides such a general expression, indicating for example that the helium B_0 values from classical theory will be too small (11, 8) by perhaps 10 per cent at 100°K. and 27 per cent at 50°K. For molecules having greater mass the temperature range accessible to measurement is progressively higher; accordingly the classical expression for B_0 requires only small correction to obtain a good approximation for the general quantum statistical mechanics expression.

The difficulty of obtaining exact B_0 values over a long temperature range from p - v - T data is due on the one hand to the decreasing precision in the results at lower temperatures, because of adsorption of the gases on the walls of the container, and on the other hand to the technical difficulties and lack of chemical stability at higher temperatures. Joule-Thomson data at low pressures provide a means of deducing values of

$$B_0 - T \frac{\delta B_0}{\delta T}$$

or, compactly expressed,

$$\left(\frac{\delta B_0/T}{\delta \frac{1}{T}} \right)$$

provided exact values of C_p^0 are available. Joule-Thomson values at low pressures are, however, extremely difficult to measure. They are usually too small, and in the case of the more reliable high pressure data recourse must be had to relatively long extrapolations; this is not a serious

problem for the higher temperatures but is difficult at low temperatures, because of the more complicated relation between the coefficient and the pressure. The use of such data for the evolution of the intermolecular potential has recently been carefully considered generally and also for helium and argon in particular (5).

Experience in correlating the existing data and in the attempt to measure values of the kind discussed above finally led to the belief that it might be possible to measure directly $\left(\frac{\delta U}{\delta v}\right)_\tau$ or $\left(\frac{\delta H}{\delta p}\right)_\tau$. Several years experience in attempting to measure the first of the two quantities (7) led to the opinion that no satisfactory results were possible, owing chiefly to the difficulty of controlling adsorptive effects. The attempt to measure the second quantity finally proved promising, and the development has passed through a number of stages. During the past year the latest form of apparatus has given very satisfying results, in the measurement not only of $\left(\frac{\delta H}{\delta p}\right)_\tau$ but also of C_p^0 . We shall discuss below the significance of the quantities measured and the apparatus used. A brief statement will also be made about a method of obtaining the magnitude of the intermolecular potential in the region close to the "boundaries" of the molecule.

SIGNIFICANCE OF THE QUANTITY $(\delta H/\delta p)_\tau$

The change of the enthalpy with pressure is virtually a direct measure of the effect of intermolecular forces in gases at low pressure. The quantity is related to the state variables v and T as follows:

$$\left(\frac{\delta H}{\delta p}\right)_\tau = v - T \left(\frac{\delta v}{\delta T}\right)_p = \left(\frac{\delta v \tau}{\delta \tau}\right)_p \quad (3)$$

where τ is used to denote the reciprocal of the thermodynamic temperature T . The letter v represents the volume of a unit of mass; H represents the sum of the internal energy, U , and the pressure-volume product, $p v$.

Using equation 1 we find the relation⁴

$$\frac{\delta v \tau}{\delta \tau} = \frac{\delta B_0 \tau}{\delta \tau} = f(\tau) \quad (4)$$

⁴ The quantity

$$\left(\frac{\delta U}{\delta v}\right)_\tau = -\left(\frac{\delta p \tau}{\delta \tau}\right)_v$$

becomes

$$-\frac{R}{(v - B_0)^2} \frac{\delta B_0}{\delta \tau}$$

The quantity $(\delta U/\delta p)_\tau$ is also interesting, but neither quantity is at present susceptible of accurate direct measurement.

which is solely a function of temperature, $f(\tau)$. It follows then that B_0 is given, where C is a constant of integration, by the equation

$$B_0 = Tf(\tau)d\tau + C \quad (5)$$

In the simplest case the right-hand member of equation 5 may be equated to equation 2 and important information deduced about the intermolecular potential W . Relation 5, however, is capable of supplying information regarding W in the more general case treated by modern statistical mechanical theory.

It should be observed, however, that experimental limitations deprive us of values of B_0 at temperatures where important information about W would otherwise be obtainable. Thus, by way of example, it would be desirable to possess exact values of B_0 for nitrogen, carbon dioxide, methane, water, etc. at temperatures up to 1000°C., but there is little likelihood that accurate measurements of $(\delta H/\delta p)_T$ can be pushed to anything approaching this value.⁵

The fact seems clear that attainable values of $(\delta H/\delta p)_T$, or equivalent information from the measurement of the Joule-Thomson effect, or p - v - T measurements can lead to only a part of the desirable information about W . The only exception to this statement is possibly in the case of those gases whose negative potential is small and for which the values of B_0 are in consequence positive over a range of temperature which is greatest for helium and progressively less for helium, hydrogen, neon.

The attempt to perfect other and independent means of securing information about W corresponding to high temperatures has achieved some success during the past year, owing to the indefatigable efforts of our colleague, Dr. I. Amdur. His method consists in measuring the scattering of neutral hydrogen atoms in the form of a beam, projected into particles of interest, at controlled velocities up to many times the particle velocities in a static gas at attainable temperatures. Quantum mechanics gives information regarding the molecular field of the test particle, the hydrogen atom. Using the scattering data the expectation is that it will be possible to compute the intermolecular field of the molecules into which the atoms are projected.

THE MEASUREMENT OF $(\delta H/\delta p)_T$

In principle a gas under constant fore pressure is allowed to expand through the resistance offered by a porous plug against a constant effluent pressure. In order that the temperature may remain unchanged, energy

⁵ Reliable values of p - v - T were obtained for water to 460°C. The time and expense involved were, however, almost prohibitive.

must be added or subtracted from the gas either (a) during the course of the pressure drop in the plug, or (b) after the gas has completed its expansion (1, 3).⁶ The measure of $(\delta H/\delta p)_T$ is the ratio of the amount of energy H divided by the attendant pressure drop for a unit of the gas, the temperature remaining invariable.

While the concept of the measurement is simple it proved, at least in our hands, very difficult to reach the precision desired. The first results of quantitative value were obtained using ammonia and carbon dioxide. The expansion took place in a fine metal capillary tube through which an electric heating current passed (6, 4).⁷ The experience gained led to the construction of an improved apparatus, in which a heater comprising in itself the porous plug was inserted in a thin-walled glass capillary. With this apparatus submerged in an oil bath, measurements were made using steam. The steam measurements were finally concluded using an all-metal device and the results were published (2). Recently a second all-metal apparatus, which embodies the ideas suggested by the experience gained, has been designed and executed. The new model is designed for use at temperatures from -180° to $400^\circ\text{C}.$; with small modifications it can be adapted for measurements to $-253^\circ\text{C}.$ or possibly lower.

DESCRIPTION OF THE APPARATUS

The essential features of the device are represented in figure 1. They consist of the calorimeter proper with its capillary 19, integrating shield 21, equalizing chamber 22, and heat guard 20, the heat ballast 16, the thermostat 8, the heat exchanger 5, the liquid air pot 25, radiation shields 2 and 3, and the vacuum case 1. The calorimeter is shown in greater detail at the right of the figure. The outer shell is the heat ballast, a floating member which assumes the temperature of the inlet gas. The temperature of the inlet gas is measured by the platinum resistance thermometer 28 placed in a super nickel tube 11. The gold leads of the thermometer pass through the heat station 27, which also possesses the temperature of the inlet gas. Because of the considerable heat capacity of the heat ballast, short-time variations of temperature can not occur.

The capillary is partially plugged with the heating element 40. Substantially all the flow-resistance of the calorimeter is produced by the heater. Because of the resulting turbulence, heat is transferred from heater to gas with a minimum thermal gradient. The experimental gas passes from the capillary into the equalizing chamber, the function of

⁶ Buckingham was the first, we believe, to appreciate the importance of embedding the heater in the plug.

⁷ Eucken, Clausius, and Berger have measured $(\delta H/\delta p)_T$ by method b, whereby air cooled by its Joule-Thomson effect was reheated to the temperature of admission to the plug.

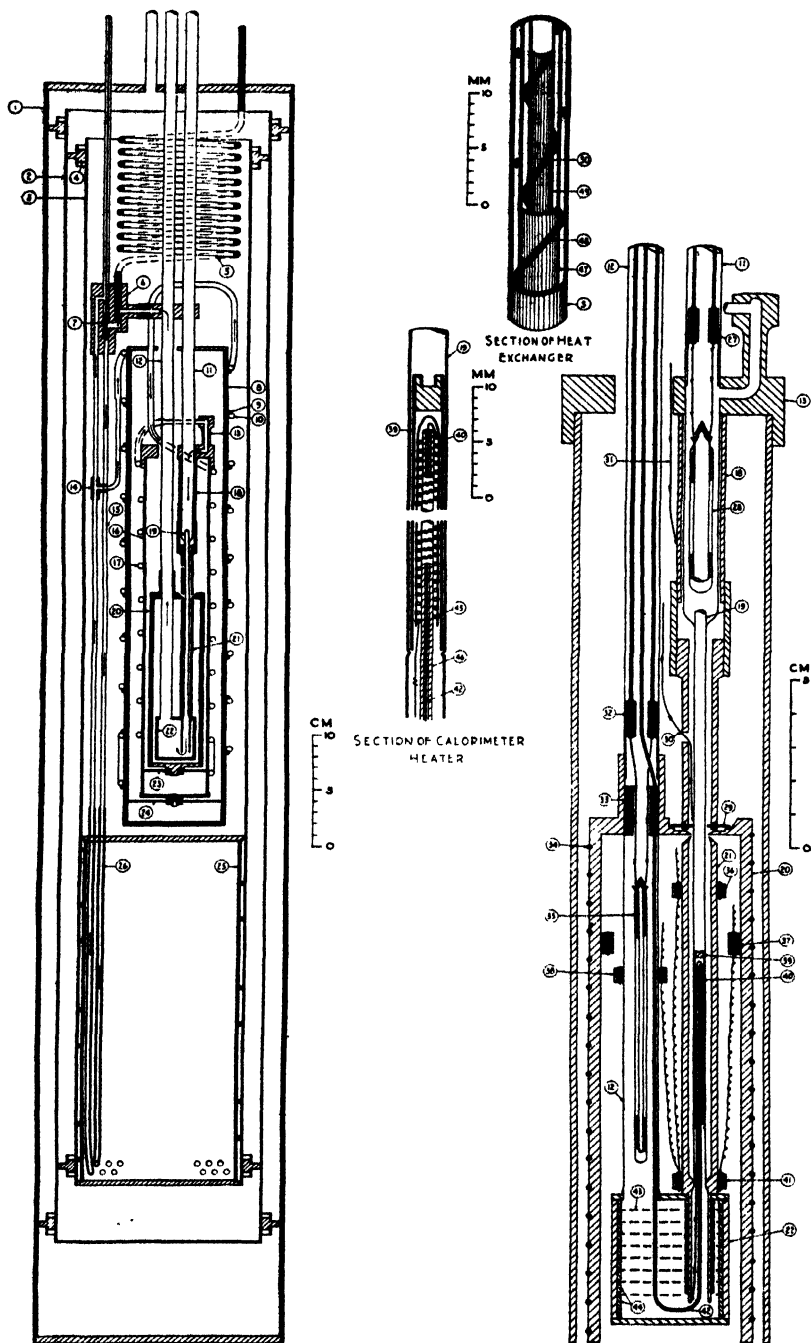


FIG. 1. Flow calorimeter for gases for measurement of the functions $(\partial H / \partial P)_T$ and $(\partial T / \partial P)_H$

which is to remove certain kinetic energy effects attendant upon the high velocity of the gas stream through the capillary and thereby to insure equality of temperature between the gas and its surroundings. The chamber is fitted with several disks of copper gauze, which are perpendicular to the gas flow and soldered to the case at their edges. The outlet temperature is measured by the platinum resistance thermometer 35. The heat guard 20 is a heavy copper vessel completely surrounding the calorimeter, except for small openings where the gas enters and leaves. It is equipped with a heater 34, by means of which its temperature may be kept the same as that of the equalizing chamber 22. A five-junction differential thermocouple with opposite junctions at 41 and 37 serves to indicate the thermal balance. The heat guard prevents exchange of heat with the surroundings by radiation and by conduction along tube 12.

The thermostat 8 consists of a copper tube 3 in. in diameter and 17 in. long, with a wall thickness of $\frac{1}{8}$ in. It surrounds the heat ballast and calorimeter. The experimental gas which flows through an 8-ft. length of $\frac{3}{16}$ in. copper tubing soldered to the outer surface of the thermostat is brought into thermal equilibrium with it. By means of a thyatron circuit arranged for phase control the temperature can be kept constant to 0.001°C . The sensitive element is a resistance thermometer which is held in good thermal contact with the thermostat. The obvious advantage of this thermostat is that all liquids are avoided and the same equipment may be used over the entire range of temperature from -180°C . to 400°C .

The heat exchanger 5, in which the incoming and outgoing streams of gas remain in approximate thermal equilibrium, conserves heat when the calorimeter is being operated at high temperatures and conserves refrigeration at low temperatures. A section of the heat exchanger is given in the enlargement at the center of the sketch. Three concentric tubes are shown. The central tube is stopped so that the gas flows in opposite directions in the two annuli. The width of each annulus is held constant by a spiral of nickel wire of the correct size. The two gas streams are thus spread out in thin layers with a thin layer of metal between them. Such an arrangement has proved to be very effective.

When the calorimeter is being operated at low temperatures, liquid air is placed in the container 25, and a certain fraction of the experimental gas is diverted from its usual channel by means of the two-way valve 7 and caused to flow through the coiled tubing 26 within the liquid air bath. Thus cooled it is mixed with the remainder of the gas stream at 14. The lower the temperature required, the greater the fraction that must be cooled.

MODE OF OPERATION AND RESULTS

The mode of use is set out completely in the paper on steam (2) but may be reviewed here very briefly. Since the quantity H is being meas-

ured, it is convenient to begin by writing a general expression for the quantity as follows:

$$H = \int_{T_0}^T C_p^0 dT + \psi_0 p + \psi_1 p^2 \cdots + h \quad (5)$$

Here

$$\psi_0 = \left(\frac{\delta B_0 \tau}{\delta \tau} \right); \quad \psi_1 = \left(\frac{\delta \varphi_1 \tau}{\delta \tau} \right)$$

from the equation of state following:

$$p = \frac{RT}{v - B}$$

$$B = B_0 + \varphi_1 p + \cdots$$

Denoting the initial condition before the gas experiences the pressure fall by the subscript i , and the final condition by f , we find

$$H_f - H_i = \int_{T_i}^{T_f} C_p^0 dT + \psi_{0f} p_f - \psi_{0i} p_i + \cdots + h \quad (6)$$

Where the fall in pressure is accompanied by an absorption of energy (cooling Joule-Thomson effect), T_i may be made equal to T_f and equation 6 becomes

$$H_f - H_i = -\psi_{0f}(p_i - p_f) - \psi_{1f}(p_i^2 - p_f^2) \dots \quad (6a)$$

A number of gases, however, exhibit a negative Joule-Thomson effect, and it would be necessary to abstract energy; this is an impossibility with the electric heater.⁸ In the former case, however, a series of measurements at various values of p_i are made for $T_f = T_i$, thereby giving the values of ψ_0, ψ_1 , etc. Measurements where $T_f > T_i$ may then be used to give values of the quantity

$$\int_{T_i}^{T_f} C_p^0 dT$$

The plan proved successful in the case of steam, where measurements were secured for p_i as low as 50 mm. and p_f as small as 6 mm. over the

⁸ It is proposed to obtain values of Ψ_0 for helium from -180°C. to as high temperatures as the apparatus permits, having in view the permeability of metals to helium. In this range Ψ_0 is positive, and it will not be possible to apply the condition $T_f = T_i$. The heat capacity is, however, known, and Ψ_1 is known from J. R. Roebuck's Joule-Thomson work to be small. At the very low pressures (1 to 4 atm.) at which the work is to be conducted, equation 6 may be used to evaluate Ψ_0 .

temperature range 39 to 125°C. The B_0 values for steam are now believed known to better than 1 per cent for 40° to 460°C. and are given by the equation

$$B_0(\text{cc. per gram}) = 1.89 - 2641.62\tau^{10^{80870\tau^2}} + \Delta B_0 \quad (7)$$

$$\Delta B_0 = 4.136 \times 10^{80}\tau^{12} - 0.543 \times 10^{60}\tau^{24}$$

When the latest form of apparatus was designed nearly two years ago we expected first to obtain B_0 values for heavy and light hydrogen, since

TABLE 1
Results of measurements on nitrogen

t	P_i	P_f	$T_f - T_i$	ψ_0	C_p	μ
°C.	atmospheres	atmospheres	degrees	joules per gram-atmosphere	joules per gram-degree	degrees per atmosphere
30.60	2.500	1.310	-0.019	0.2144		
30.61	2.501	1.309	+0.007	0.2096		
30.61	2.573	1.310	+0.002	0.2118		
30.86	2.501	1.309	+0.365	0.2128		
				0.2122 (Av.)		
30.86	2.501	1.309	+0.365	0.2122	1.036	0.2048
30.81	2.501	1.309	+1.252	0.2122	1.035	0.2050
					1.033*	0.2055†
42.67	2.559	1.021	+0.022	0.1990		
42.91	2.558	1.021	+0.249	0.2072		
				0.2031 (Av.)		
42.91	2.558	1.021	+0.249	0.2031	1.026	0.1980
43.29	2.521	1.000	+1.072	0.2031	1.045	0.1944
					1.033*	0.1890†
75.18	2.543	1.308	+0.027	0.1621		
75.01	2.547	1.309	+0.026	0.1591		
				0.1606 (Av.)		
75.18	2.547	1.309	+0.357	0.1606	1.031	0.1588
75.78	2.547	1.309	+1.555	0.1606	1.053	0.1525
					1.034*	0.1505†

* Partington and Shilling: *The Specific Heats of Gases*, p. 145. D. Van Nostrand Co., New York (1924).

† Values taken from Roebuck and Osterberg (*Phys. Rev.* **48**, 450 (1935)).

these values would provide data for testing the quantum statistical mechanical expression for B_0 . (Recently, however, values have been published by K. Schäfer (10).) A few preliminary measurements for hydrogen have been completed. However, owing to the need of accurate B_0 values for nitrogen on the part of Professor Beattie and his group for use in reducing a large body of gas thermometry data, measurements on nitrogen were undertaken. The results obtained (table 1) are not definitive values but

represent fairly what may be expected by way of consistency in the measurement of ψ_0 , C_p , and the Joule-Thomson coefficient μ .

REFERENCES

- (1) BUCKINGHAM, EDGAR: *Phil. Mag.* **6**, 519 (1903).
- (2) COLLINS, S. C., AND KEYES, F. G.: *Proc. Am. Acad. Arts Sci.* **72**, 283 (1938).
- (3) DAVIS, H. N.: *Phys. Rev.* **5**, 659 (1915).
- (4) EUCKEN, A., CLAUSIUS, K., AND BERGER, W.: *Z. tech. Physik* **13**, 267 (1932).
- (5) HIRSCHBERGER, J. O., EWELL, R. B., AND ROEBUCK, J. R.: *J. Chem. Phys.* **6**, 205 (1938).
- (6) KEYES, F. G., AND COLLINS, S. C.: *Proc. Natl. Acad. Sci. U. S.* **18**, 328 (1932).
- (7) KEYES, F. G., AND SEARS, FRANCIS: *Proc. Natl. Acad. Sci. U. S.* **2**, 38 (1925).
- (8) KIRKWOOD, J. G.: *Physik. Z.* **33**, 39 (1932).
- (9) PALEY, R. E. A. C., AND WIENER, NORBERT: *Am. Math. Soc. Coll. Pub.* **XIX**, 1934, Chap. III.
- (10) SCHÄFER, K.: *Z. physik. Chem.* **B36**, 85 (1937); **B38**, 187 (1937).
- (11) UHLENBECK, G. E., AND BETH, E.: *Physica* **3**, 729 (1936).

INTERMOLECULAR FORCES AND THE PROPERTIES OF GASES¹

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The equation of state for gases is intimately connected with the law of force between the individual molecules. We are interested in making this relationship explicit. From a set of accurate measurements of PVT or Joule-Thomson coefficients, we should obtain the energy of interaction, $E(r)$, of a pair of molecules separated by a distance r . Or, conversely, if $E(r)$ is calculated from the quantum-mechanical perturbation equations, we should derive the corresponding equation of state. Fowler (6), Lennard-Jones (14), and others have expressed the second virial coefficient in terms of $E(r)$, so that the experimental data at low pressures determine the interaction energy. However, the experimental difficulties in obtaining the imperfections of gases accurately at low pressures restrict the use of this method of analysis to a comparatively few simple substances which have been studied with extraordinary care. For this reason, it is desirable to perfect an equation of state which is fairly accurate for high pressures and which still can be interpreted in terms of the intermolecular forces. In this paper we consider first what information can be obtained from experimental data at low pressures and then that from data at high pressures.

I. INTERPRETATION OF LOW-PRESSURE DATA

The equation of state for gases at reasonably low pressures can always be written in the form (6, 27):

$$pV = RT \left(1 + \frac{B'(T)}{V} + \frac{C'(T)}{V^2} + \frac{D'(T)}{V^3} + \cdots \right) \quad (1)$$

where $B'(T)$, $C'(T)$, $D'(T)$ are functions of temperature but not of pressure. These are usually referred to as the second, third, fourth . . . virial coefficients, respectively. There is some ambiguity in the literature as to the definition of the virial coefficients, but in the course of this paper we shall always define them with reference to equation 1. The interpretation

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of these virials in terms of the law of force between a pair of molecules was carried out by Ursell (27), Fowler (6), and others so that we can write:

$$B'(T) = 2\pi N \int_0^\infty r^2 \left(1 - e^{\frac{-E(r)}{kT}} \right) dr \quad (2)$$

Here $E(r)$ is the energy of interaction of a pair of molecules separated by a distance r , k is the Boltzmann constant, and N is Avogadro's number. The derivation of this formula requires that the collisions between the molecules be treated according to classical mechanics. We wish to consider equation 2 as an integral equation for the determination of $E(r)$. If we knew $B'(T)$ over a large temperature range, we should be able to determine $E(r)$ with some precision. Lennard-Jones (14) made a real contribution to the study of gases when he showed how to perform the integration in equation 2 on the assumption that

$$\begin{aligned} E(r) &= - \left[(r_0/r)^6 - \left(\frac{r_0}{r} \right)^s \right] E_m \frac{s}{s-6} \left(\frac{s}{6} \right)^{6/s-6} \\ &= - c/r^6 + l/r^s \end{aligned} \quad (3)$$

This form for the potential is roughly what we would expect on the basis of quantum mechanics. Here r_0 is the separation for which the potential is zero, and E_m is the energy required to separate the molecules from their equilibrium separation. Substituting the Lennard-Jones potential into equation 2 we obtain

$$B'(T) = b_0 F_s \left(\frac{E_m}{kT} \right) \quad (4)$$

where b_0 is the van der Waals b for molecules with a diameter r_0 (i.e., $b_0 = \frac{2}{3}\pi N r_0^3$) and F_s is a function of E_m/kT , which Lennard-Jones has tabulated for different values of s . It has not been possible to determine s accurately from the experimental data, since the curves corresponding to different values of s have nearly the same shape. For many substances the indications seem to point to a value of s in the neighborhood of 12, and we shall use this in our analysis. Figure 1 shows $B'(T)$ or F_{12} plotted as a function of E_m/kT . This form for the second virial coefficient is valid for all substances to which this Lennard-Jones potential applies.

It is interesting to examine the van der Waals constants which would be obtained for molecules obeying this inverse twelfth-power repulsion and inverse sixth-power attraction law. Expanding van der Waals' equation in powers of $1/V$ it is easy to show that $B'(T)$ should equal $b - a/RT$. From this relationship a and b might be determined from the experimental second virial coefficient. Plotting $B'(T)$ against $1/T$ (as in figure 1), a straight line would be drawn through the experimental points and the

intercept for $1/T = 0$ would be the value of b . From the curvature of F_{12} it follows that if the experimental data are given for high temperatures, the value of b obtained will be considerably smaller than b_0 , while low-temperature observations will yield a much larger value for b . Table 1

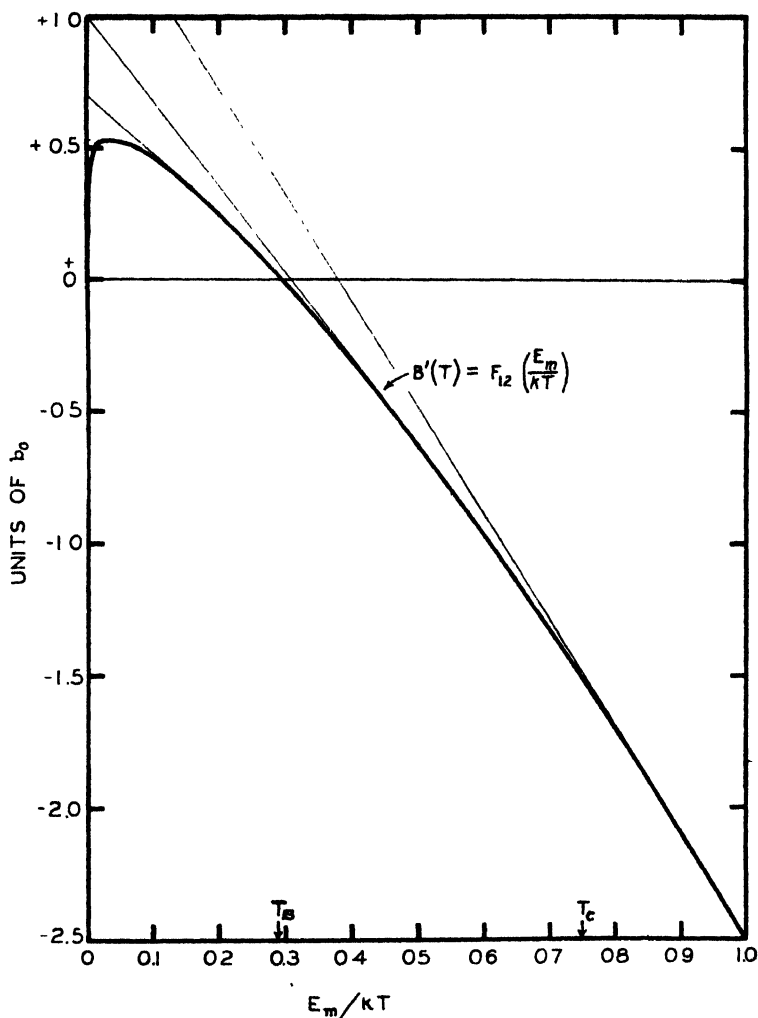


FIG. 1. Second virial coefficient as a function of temperature

shows the temperature variations of a and b obtained in this manner. Since these experimentally determined a and b change by almost a factor of 2 in going from the critical temperature to the low-pressure Boyle point (i.e., the temperature at which $B'(T) = 0$), we should not think of them as constants.

The Beattie-Bridgeman equation (1, 2, 3, 4) is perhaps the best empirical equation for representing the p , V , T for gases up to pressures of the order of 100 atm. Here:

$$pV^2 = RT(1 - c/(VT^3))(V + B_0 - bB_0/V) - A_0(1 - a/V) \quad (5)$$

And, expanding the right-hand side in powers of V , it follows that

$$B'(T) = B_0 - A_0/RT - c/T^3 \quad (6)$$

This expression for the second virial coefficient agrees with the second virial coefficient obtained from the Lennard-Jones potential over a wide temperature range, if c has the proper value with respect to B_0 and A_0 . Let us suppose for the time being that the molecules which we are considering actually obey the Lennard-Jones potential with the inverse twelfth-power repulsive and inverse sixth-power attractive energy and that our gas has been studied in a temperature range lying roughly between the critical

TABLE 1
Temperature variations of a and b

E_m/kT	b/b_0	$a/E_m b_0 N$	
0.893	1.616	4.154	T_c , critical temperature
0.709	1.272	3.717	
0.563	1.072	3.397	
0.448	0.943	3.141	T_B , Boyle point (low pressure)
0.355	0.861	2.934	
0.282	0.801	2.743	
0.224	0.754	2.555	
0.178	0.716	2.363	

temperature and the low-pressure Boyle point. Then we expect equations 4 and 6 to agree at the three temperatures corresponding to $E_m/kT = 0.7906$, 0.4989, and 0.2924, from which it follows:

$$E_m = 0.04127 \times 10^{-15} A_0 / (R B_0) \text{ ergs} \quad (7a)$$

$$b_0 = 1.249 B_0 \quad (7b)$$

Now, there is a third relationship between c and the constants A_0 and B_0 which is fulfilled *only if the molecules actually satisfy the Lennard-Jones potential*:

$$c = 0.0236 A_0^2 / (R^2 B_0^3) \quad (7c)$$

Equation 7c can therefore be used as a test for the validity of this potential energy function. Table 2 compares the values of E_m and of b_0 calculated from equations 7a and 7b with the values given by Lennard-Jones (15). Here we use the values for the constants given by Beattie and Bridgeman

(4). In the last two columns we compare the values of c calculated by equation 7c with the values observed. The agreement is good for neon, argon, nitrogen, and carbon monoxide and fairly good for hydrogen, oxygen, carbon dioxide, nitrous oxide, and methane. However, it is poor for helium, ethylene, ammonia, and diethyl ether. Most probably the constants for the helium were fitted at a temperature very high compared to the critical point, and so our method of calculating the molecular constants for helium is not justifiable. Ammonia may be partially polymerized.

The Lennard-Jones potential is quite satisfactory for the analysis of the experimental second virial coefficients, but not quite accurate enough to

TABLE 2
Values of b_0 , E_m , and c

GAS	b_0 (CALCULATED FROM BEATTIE- BRIDGEMAN)	b_0 (CALCULATED FROM LENNARD- JONES)	E_m (CALCULATED FROM BEATTIE- BRIDGEMAN)	E_m (CALCULATED FROM LENNARD- JONES)	c (CALCULATED FROM EQUATION 7c)	c (OBSERVED)	AGREEMENT
	cc. per mole	cc. per mole	ergs	ergs	liters per degree ³ mole	liters per degree ³ mole	
Ne	25.73	26.04	5.19×10^{-15}	4.881×10^{-15}	966	1,010	Good
A	49.10	50.02	16.51	16.50	59,400	59,900	
N ₂	63.02	64.94	13.40	13.24	40,700	42,000	
CO	63.02		13.40	13.36	40,700	42,000	
H ₂	26.18	31.41	4.74	4.246	749	504	Fair
O ₂	57.75		16.22	16.97	66,200	48,000	
CO ₂	130.85		24.03		488,000	660,000	
N ₂ O	130.85		24.03		488,000	660,000	
CH ₄	69.78		20.49	19.70	161,000	128,000	Poor
He	17.49	21.41	0.776	0.950	2.19	40	
C ₂ H ₄	151.8		25.45		673,000	227,000	
NH ₃	42.65		35.24		502,000	4,769,000	
(C ₂ H ₅) ₂ O	567.6		34.61		6,325,000	333,000	

fit the Joule-Thomson coefficients of Roebuck and his coworkers (21, 22, 23, 24). The Joule-Thomson coefficients can be obtained with great accuracy, since they involve only a measurement of temperature and pressure. The second virial coefficients are accurate to several significant figures less than the pressure-volume data from which they are obtained. It was shown in a previous communication (10) that the Joule-Thomson coefficient extrapolated to zero pressure, μ_0 , is simply related to the second virial coefficient:

$$\mu_0 = \frac{T^2}{R + C_v} \frac{d}{dT} \left(\frac{B'(T)}{T} \right) \quad (8)$$

where C_v^0 is the specific heat at constant volume extrapolated to zero pressure. C_v^0 can be calculated very accurately for many substances from

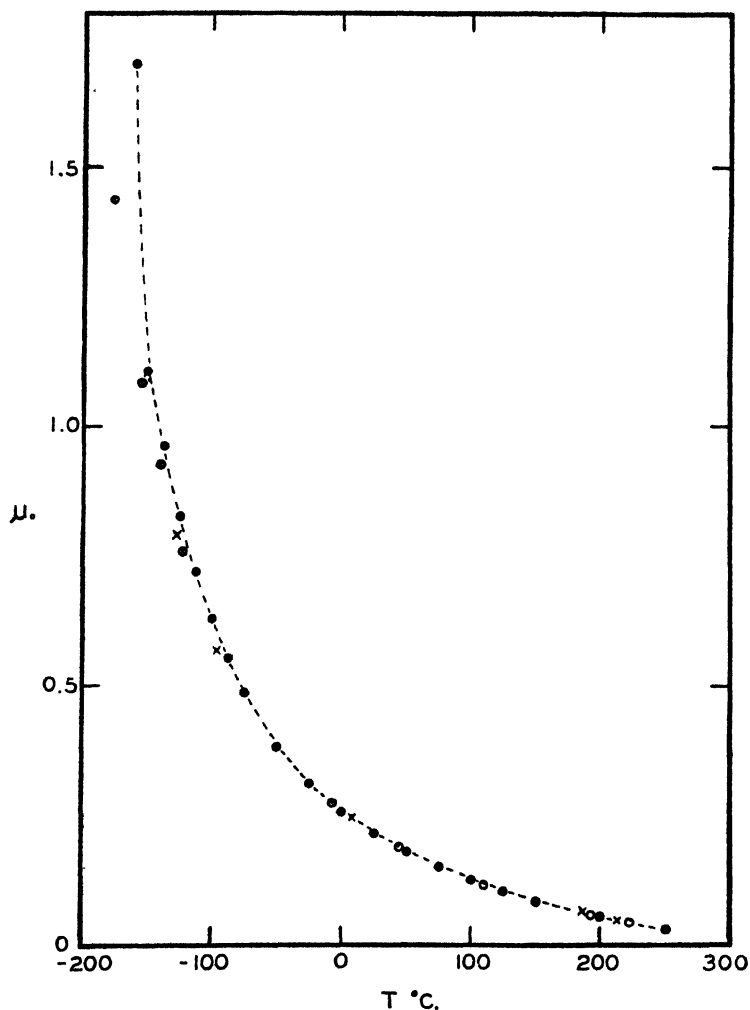


FIG. 2. Nitrogen: Joule-Thomson coefficient extrapolated to zero pressure. ●, experimental observations by Roebuck and Osterberg; ○, calculated Lennard-Jones potential, $s = 12$; ×, calculated Lennard-Jones potential, $s = 9$.

an analysis of the spectroscopic energy levels. Substituting equation 4 into equation 8 we obtain the relation:

$$\mu_0 = \frac{b_0}{R + C_v^0} G_s(E_m/kT) \quad (9)$$

Here the $G_s(E_m/kT)$ are functions of temperature which have been tabulated for different values of s . The determination of the two constants b_0 and E_m is a simple job in curve fitting. For the case of nitrogen, we used the spectroscopically determined specific heat values of Trautz and Ader (26) in equation 9. Figure 2 shows the agreement which is obtained between the calculated Joule-Thomson coefficients and the values measured by Roebuck and Osterberg (23). The best values for b_0 and E_m were as follows:

	b_0	E_m
	cc.	ergs
$s = 9$	73.3	9.95×10^{-15}
$s = 12$	64.9	13.24

These are the same as the values obtained by Lennard-Jones from his analysis of the second virial coefficients (14). It will be noticed that the calculated and observed values agree well for the high-temperature region, but the calculated values are too small at lower temperatures. If the two constants were chosen so that the fit was good for both the high and the low temperatures, it would be unsatisfactory in the intermediate region. We believe that a more accurate potential curve, perhaps one in which the repulsion varies exponentially with the separation, would give a better fit.

Gaseous mixtures are the simplest example of chemical solutions, and they should be useful in studying the laws of mixing and the interactions between unlike molecules. We can apply the same method of analysis to these mixtures that we used for the pure components. The laws of mixing at low pressures are well known (6). If we let N_1 and N_2 be the mole fractions of components 1 and 2,

$$(C_v^0)_{\text{mix.}} = N_1(C_v^0)_1 + N_2(C_v^0)_2 \quad (10)$$

and

$$B'(T)_{\text{mix.}} = N_1^2 B'(T)_1 + 2N_1 N_2 B'(T)_{12} + N_2^2 B'(T)_2 \quad (11)$$

where $B'(T)_{12}$ is the second virial coefficient concerned with the collision of unlike molecules. It differs from the coefficient for pure components (2), only in having $E(r)_{12}$, the energy between unlike molecules, in place of $E(r)$. Substituting equations 10 and 11 into equation 8 for the Joule-Thomson coefficient:

$$\mu_{\text{mix.}}^0 = \frac{N_1^2 [(C_v^0)_1 + R] \mu_1 + N_2^2 [(C_v^0)_2 + R] \mu_2 + 2N_1 N_2 A_{12}}{R + N_1 (C_v^0)_1 + N_2 (C_v^0)_2} \quad (12)$$

Here

$$A_{12} = -2\pi N \int_0^\infty r^2 \left[1 - \left(1 - \frac{E(r)_{12}}{kT} \right) e^{-\frac{E(r)_{12}}{kT}} \right] dr \quad (13)$$

And, using the Lennard-Jones type of potential,

$$A_{12} = (b_0)_{12} G_s((E_m)_{12}/kT) \quad (14)$$

The analysis of the law of force between two unlike molecules then consists in solving equation 12 for A_{12} for many different values of the temperature. These experimental values of A_{12} serve to determine the $(b_0)_{12}$ and $(E_m)_{12}$ of equation 14. For each mixture we obtain a different value for A_{12} at a particular temperature. The consistency of the experimental data is then demonstrated by the agreement or disagreement of these values obtained from different mixtures. The law of mixtures has been derived from rigorous statistical mechanical considerations, so that any disagreement must be due either to experimental errors or to factors which have not been taken into account in this treatment. We examined the experimental Joule-Thomson coefficients for mixtures of helium and nitrogen measured by Roebuck and Osterberg (24). The spread in the experimental A_{12} is large, and it is difficult to make an accurate analysis. We obtained the best agreement with the experimental data when the collision diameter for the unlike molecules, $(r_0)_{\text{He-N}_2}$, was taken to be the arithmetical mean of the collision diameters for the pure components, i.e.,

$$\begin{aligned} (r_0)_{\text{He-N}_2} &= 1/2((r_0)_{\text{He}} + (r_0)_{\text{N}_2}) \\ &= 1/2(2.57 + 3.72) = 3.15\text{\AA}. \end{aligned}$$

and the coefficient of van der Waals attraction for the unlike molecules, $c_{\text{He-N}_2}$, was taken to be the geometrical mean of the coefficients for the pure components,² i.e.,

$$\begin{aligned} c_{\text{He-N}_2} &= (c_{\text{He}}c_{\text{N}_2})^{1/2} = (0.1522 \times 14.0)^{1/2} \times 10^{-59} \\ &= 1.46 \times 10^{-59} \text{ ergs-cm.}^6 \end{aligned}$$

Figure 3 compares the calculated and observed Joule-Thomson coefficients for the four mixtures studied. It is only in the case of mixture No. 1 that the discrepancy is large. An error of 1 per cent in the quantitative analysis of the mixture would be sufficient to account for the difference. In any event, $(r_0)_{\text{He-N}_2}$ is determined within 2 per cent and $c_{\text{He-N}_2}$ within 10 per

² J. Corner, an associate of Lennard-Jones, has pointed out to us in a private communication that the Slater-Kirkwood formulation of the coefficient of van der Waals attraction between unlike molecules would lead to a value of $c_{\text{N}_2-\text{He}}$ within 1 per cent of the geometrical mean. For other mixtures he might not expect this law to hold so accurately.

cent for the potential between the unlike molecules. This type of interaction between unlike molecules has been utilized extensively by Hildebrand (8) in his work on the solubilities of non-polar substances.

We attempted to make a similar analysis of mixtures of argon and helium, which have also been studied by Roebuck and Osterberg (work unpublished). In this case, the A_{12} obtained from different mixtures had systematic variations, so that no definite conclusions could be reached. The discrepancy might be attributed to an unmixing of the gases in passing through the porous plug, although this explanation seems very unlikely.

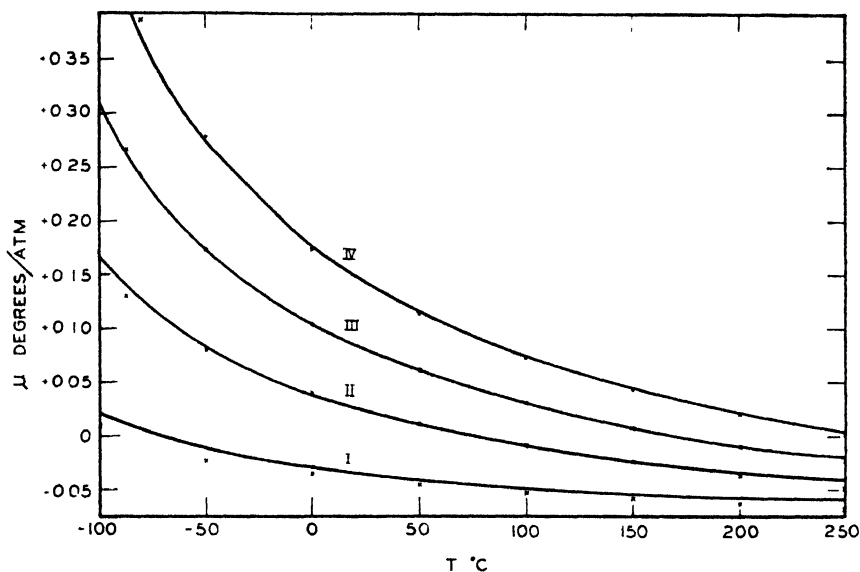


FIG. 3. Helium-nitrogen mixtures: Joule-Thomson coefficient extrapolated to zero pressure. —, experiments of Roebuck and Osterberg; X, calculated values. Curve I, mixture No. 1, 75.5 per cent helium; curve II, mixture No. 2, 51.0 per cent helium; curve III, mixture No. 3, 33.2 per cent helium; curve IV, mixture No. 4, 16.6 per cent helium.

II. A LIMITING EQUATION OF STATE FOR HIGH TEMPERATURES

As the temperature becomes high compared to the critical temperature we might suppose that the equation of state for a gas would approach some simple limiting form. Experimentally, it is found that at sufficiently high temperatures the internal energy of a gas at constant temperature is a linear function of the density. Michels, Bijl, and Michels (19) have found that this is true for carbon dioxide up to pressures of 3000 atm., where the Beattie-Bridgeman equation no longer applies (20). The black lines in figure 4 show the results of measurements of Michels, Bijl, and Michels. The circles are points calculated from the Beattie-Bridge-

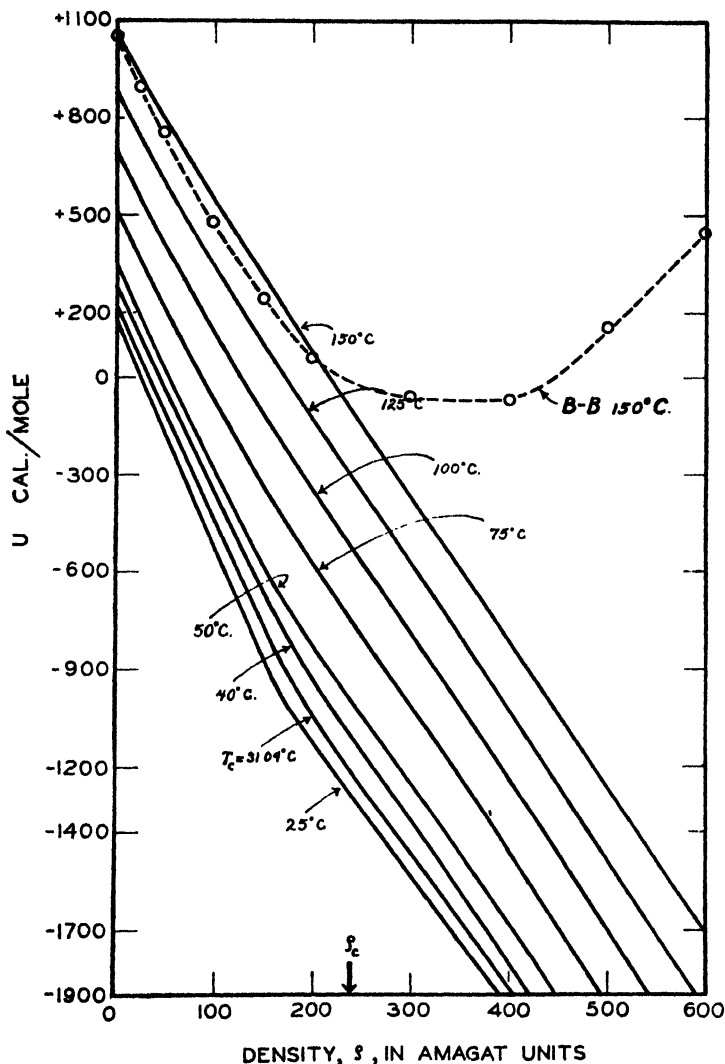


FIG. 4. Carbon dioxide: internal energy as a function of density

man equation for a temperature of 150°C . For this equation of state, the internal energy, U , has the form:

$$U_1^1 = U_0(T) - (A_0 + 3Rc/T^2)/V - 1/2(-aA_0 + 3RcB_0/T^2)/V^2 + RcbB_0/(T^2V^3) \quad (15)$$

At high temperatures it approaches the form:

$$U = U_0(T) - A_0(1 - 1/2a/V)/V \quad (16)$$

This expression would give the best agreement with the experimental data at the high temperatures if a were taken to be 0. The internal energy cannot keep on decreasing with increasing density, but perhaps the correction factor should be introduced as an exponential with volume, as has been pointed out by Kincaid and Eyring (13). Our present difficulty is that we do not know how to interpret the Beattie-Bridgeman constants, a and b , in terms of the intermolecular forces. However, if we take the internal energy to be a linear function of the density, we are led to a simple equation of state which has a simple interpretation on the basis of the Menke probability functions (18).

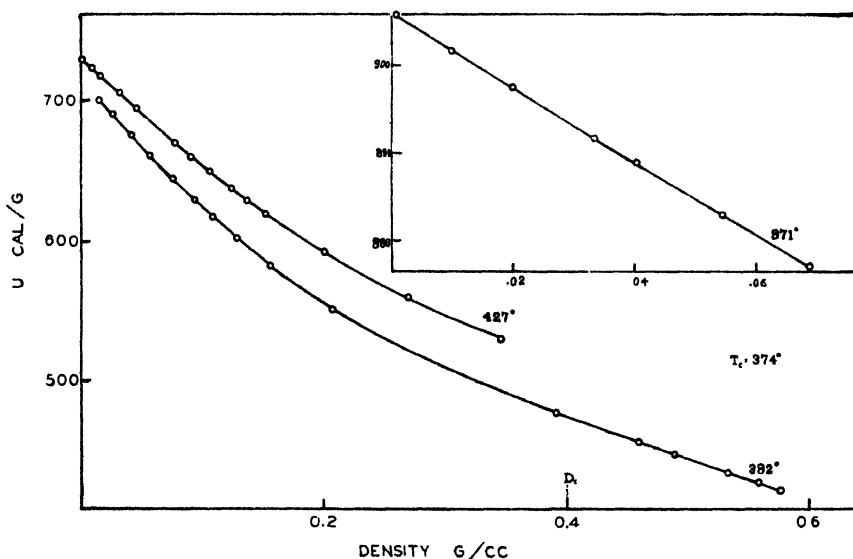


FIG. 5. Steam: internal energy as a function of density

For pressures in the neighborhood of 100 atm. the Beattie-Bridgeman equation is excellent. Up to pressures of this magnitude at high temperatures, this equation gives the internal energy to be very nearly a linear function of the density. In figure 5 we have plotted the measurements of Keenan and Keyes (12) for the internal energy of steam as a function of density for various temperatures. At the high temperatures we obtain accurate straight lines. For temperatures near the critical point there are deviations. The experimental values of Roebuck for air (21) provide another example where the internal energy is a linear function of the density. This relationship requires that $\left(\frac{\partial U}{\partial \frac{1}{V}}\right)_T$ be a constant independent

of pressure for each temperature. Table 3 shows that this is true within the irregular variations of the data.

At low temperatures the linearity of the internal energy with density still holds for all dilute gases. Hildebrand (8) has shown that it is also true for the so-called "normal liquids." We do not know whether the internal energy of these liquids lies along the same straight line as the internal energy of the gas. In figure 6 we have plotted the internal energy of *n*-butane in the temperature range lying between the critical temperature and the ordinary boiling point (from the work of Sage, Webster, and Lacey (25)). The fact that the internal energy of the liquid has a different slope from that of the gas in the cases of water and of butane may be due to hindered rotation in the condensed phase. Many liquids must be studied in this manner before any definite conclusions can be reached.

TABLE 3
Values of $\left(\frac{\partial U}{\partial \frac{1}{V}}\right)_T$ for air

<i>P</i>	-75°C.	-50°C.	50°C.	100°C.	200°C.
<i>atm.</i>					
1	1767	1618	1606	1498	1429
20	1685	1673	1510	1529	1400
60	1692	1693	1601	1544	1380
100	1712		1499	1574	1392
140	1753	1603			
180		1576			

The deviations in the critical region can be explained on the basis of fluctuations. In the vicinity of the critical point it follows from statistical mechanics that there is almost the same probability that in a small unit of volume at any instant there will be *n* molecules more than the average as that there will be *n* molecules less than the average. But the dense regions give disproportionately large negative contributions to the internal energy. We know from opalescence and related effects that the fluctuations in the critical region are large. Perhaps the most pertinent evidence is obtained through the specific heat at constant volume. Gibbs has shown that quite generally,

$$C_v = \frac{\overline{(U - \bar{U})^2}}{RT^2}$$

where *U* is the instantaneous value of the internal energy and the bars represent the time averages (6). Thus *C_v* is a direct measure of the fluctuations in the internal energy. Michels, Bijl, and Michels (19) find

that the specific heat at constant volume of carbon dioxide has a sharp maximum at the critical point. Quantitative estimates of the effect of these fluctuations are of the right order of magnitude to explain the devia-

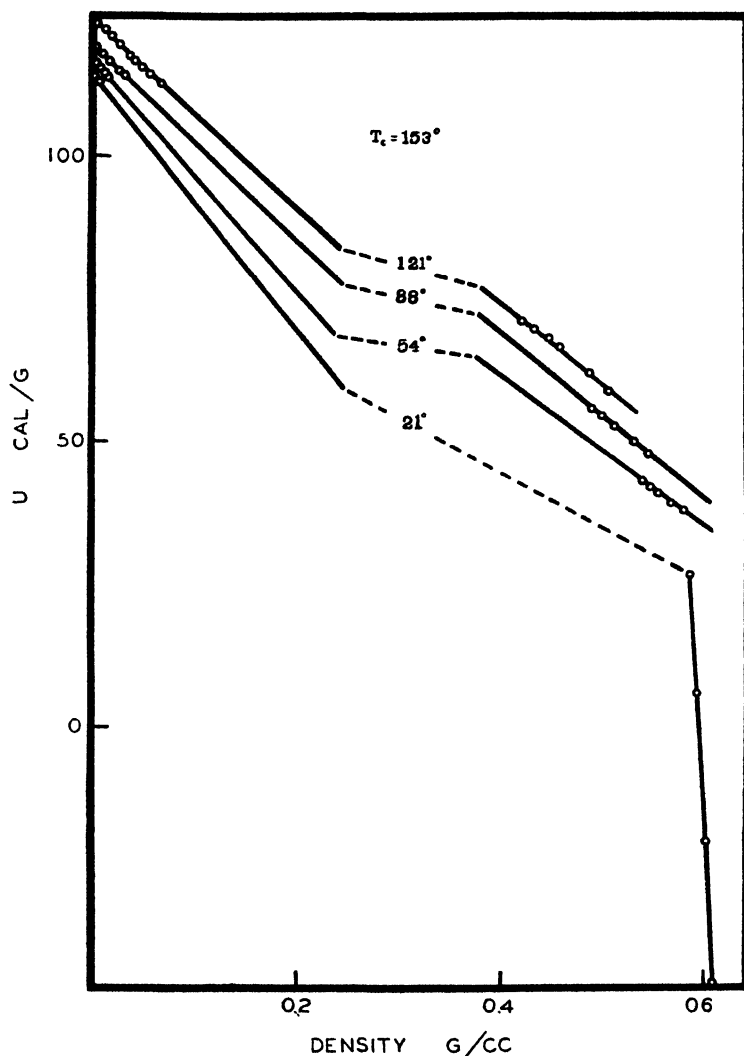


FIG. 6. n -Butane: internal energy as a function of density

tions from the linearity of the internal energy with density. The constants in the Beattie-Bridgeman equation are chosen so that the equation of state fits the experimental data in this region in spite of the fluctuations. Such a choice of constants is certainly desirable from a practical standpoint,

but it makes it more difficult to interpret these constants in terms of the molecular forces, than if they were chosen to fit a temperature range where fluctuations are unimportant.

Suppose that the internal energy, U , is a linear function of the density, i.e.,

$$U = - \frac{RT^2}{V} \frac{dB'(T)}{dT} + U_0(T) \quad (17)$$

For the time being, $B'(T)$ could be a general function of temperature, but we will soon identify it with the second virial coefficient defined in equation 1. From thermodynamics we know that

$$U = - T^2 \left(\frac{\partial}{\partial T} (A/T) \right)_v \quad (18)$$

where A is the maximum work function. Combining equations 17 and 18 and integrating with respect to the temperature, keeping the volume constant, we obtain the relation for A :

$$A = + \frac{RTB'(T)}{V} - T \int \frac{U_0(T)}{T^2} dT - RT \int \left[\frac{1}{V} + \frac{f(V)}{V^3} \right] dV \quad (19)$$

The last term is the constant of integration. Now, using this expression for A in the thermodynamical equation of state,

$$p = - \left(\frac{\partial A}{\partial V} \right)_T = \frac{RT}{V} \left[1 + \frac{B'(T)}{V} + \frac{f(V)}{V^2} \right] \quad (20)$$

For large specific volumes the equation of state must reduce to the virial equation 1 and this gives a positive proof that $B'T$ in equations 17 to 20 is actually the second virial coefficient. The linearity of the internal energy with density is equivalent to the temperature independence of the third, fourth, etc. virial coefficients.

The form for $f(V)$ can be obtained explicitly on the assumption that it is the same as for rigid non-attracting spheres. At very high temperatures where $E_m \ll kT$, the molecules approach this ideal and equation 20 should still apply. Under these conditions Happel (7) has evaluated the third and fourth virial coefficients in terms of the space in which the hard spheres overlapped. He obtained $C' = 0.625b^2$ and $D' = 0.2869b^3$, where b is the van der Waals constant corresponding to a rigid collision diameter, r . Hirschfelder, Stevenson, and Eyring (10) showed that asymptotically, as the molecules become very close packed, the van der Waals or the Happel equation becomes:

$$(p + a/V^2)(V - 0.7163b^{1/3}V^{2/3}) = RT \quad (21)$$

Here the constant 0.7163 is a geometrical factor made up of pure numbers such as π , $\sqrt{2}$, etc., calculated on the assumption that the molecules are packed into a body-centered lattice; face-centered packing would have led to a value of 0.6962 instead. The requirement that Happel's equation should agree with equation 21 throughout the liquid range of densities serves to evaluate the fifth virial coefficient. Comparing this virial equation with equation 20 we obtain the equation:

$$p = \frac{RT}{V} (1 + B'(T)/V + 0.625b^2/V^2 + 0.2869b^3/V^3 + 0.1928b^4/V^4) \quad (22)$$

This relation follows as a direct consequence of the linearity of the internal energy with density, and the assumption that at sufficiently high temperatures the molecules behave like rigid non-attracting spheres. This equation of state differs from that of Hirschfelder, Stevenson, and Eyring (10) only in the form of the second virial coefficient.

The Joule-Thomson coefficient as a function of pressure provides a very sensitive test for the validity of equation 22. At zero pressure μ_0 is a function only of the second virial coefficient; at high pressure the Joule-Thomson coefficient depends on all of the virial coefficients in an important way. From simple thermodynamical considerations:

$$\mu = \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] / \left[C_v - T \left(\frac{\partial V}{\partial T} \right)_p^2 / \left(\frac{\partial V}{\partial p} \right)_T \right] \quad (23)$$

And from equation 22 it follows that:

$$C_v = C_v^0 - \frac{RT}{V} \frac{d^2(TB'(T))}{dT^2} \quad (24)$$

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{V}{T} \frac{\left[p + \frac{RTB'(T)}{V^2} + \frac{RT}{V^2} (R + C_v^0) \mu_0 \right]}{\left[p + \frac{RTB'(T)}{V^2} - RT \frac{d}{dV} \left(\frac{f(V)}{V^2} \right) \right]} \quad (25)$$

$$\left(\frac{\partial V}{\partial p} \right)_T = -V \left[p + \frac{RTB'(T)}{V^2} - RT \frac{d}{dV} \left(\frac{f(V)}{V^2} \right) \right]^{-1} \quad (26)$$

Here, of course, we have abbreviated

$$\frac{f(V)}{V^2} = 0.625 \frac{b^2}{V^2} + 0.2869b^3/V^3 + 0.1928b^4/V^4 \quad (27)$$

We can compare the results of this equation with the experimental Joule-Thomson coefficients for argon obtained by Roebuck and Osterberg (22). In a previous communication, we found a potential energy function, $E(r)$, from which we calculated μ_0 in agreement with the experimental values.

This potential energy also served to evaluate $B'(T)$. Therefore when we consider the Joule-Thomson coefficient at high pressures, the only constant which we can adjust is the value of van der Waals b . Figure 7 compares the experimental Joule-Thomson coefficients of Roebuck and Osterberg with the values which we calculate on the assumption first that $b = 40$

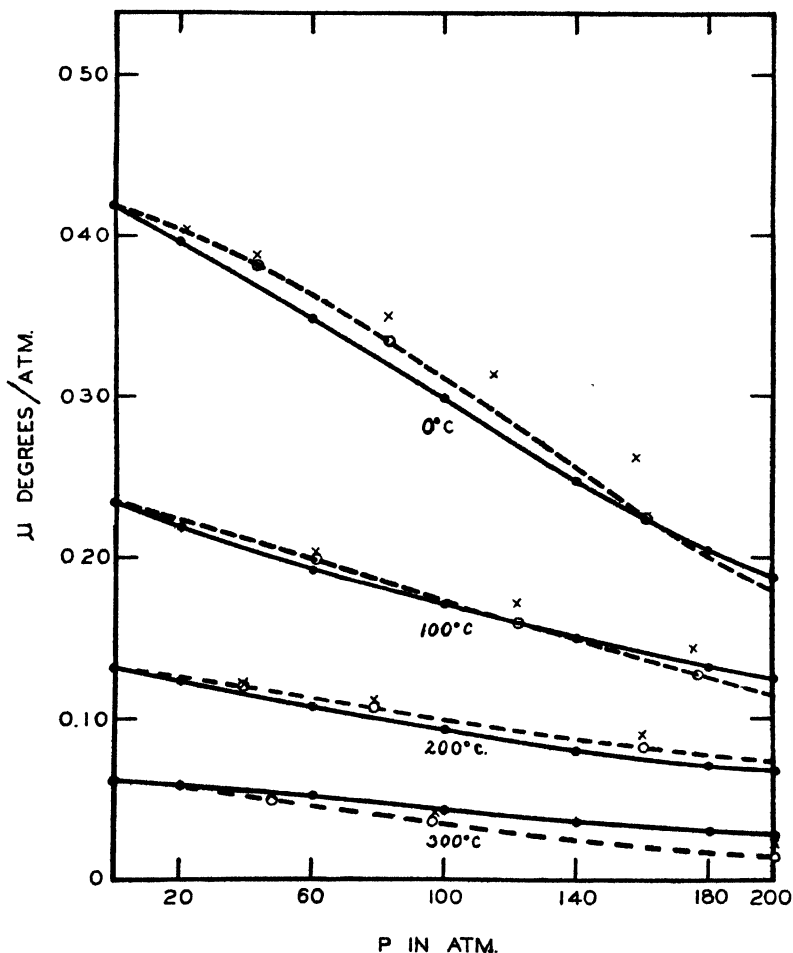


FIG. 7. Argon: Joule-Thomson coefficient. \circ , calculated, $b = 40$ cc.; \times , calculated, $b = 35$ cc.; \bullet , observed by Roebuck and Osterberg.

cc. and then that $b = 35$ cc. For $b = 40$ cc. the agreement of the calculated with the experimental values is surprisingly good. However, it is clear that a slightly smaller value of b would give better agreement at the higher temperatures and a slightly larger value for b is indicated for the lower temperatures. Van der Waals' b for argon, calculated in the manner

of the first section from low-pressure measurements, is 37 cc. for 300°C. and 47 cc. for 0°C. From the Cailletet and Mathias relationship considering the liquid to be close packed, $b = 41.2$ cc. The critical constants give $b = 32.3$. Thus the value of $b = 40$ cc., which the experimental Joule-Thomson coefficients indicate, is in accord with the value of b determined by the usual methods. The van der Waals b which we have used corresponds to the molecules having collision diameters 7 per cent smaller than the diameter at which their energy of repulsion exactly compensates the energy of attraction. We conclude from the above analysis: (1) The assumption that the third and higher virial coefficients are constants provides a good first approximation. (2) The values of the third and higher virial coefficients can be closely linked with the collision diameters or van der Waals b , and the values thus obtained are in close agreement with the results of other experiments.

Up to this point, our approach to the equation of state has been from the standpoint of pure thermodynamics. Now let us examine the significance of the linearity of the internal energy with density from the standpoint of the individual molecular interactions. There are two methods of doing this, which have become almost standard practice in statistical mechanics. First, we might think of all of the molecules except one being held in their mean positions and study the effective, or the free, volume in which this one molecule can move. The second method also fixes our attention on one molecule, but here we are interested in the instantaneous distribution of molecules in the vicinity of our chosen one. This distribution leads to the well-known Menke probability function (18), which may be evaluated from x-ray diffraction patterns.

The free volume, V_f , may be defined by means of the partition function:

$$F^N = [V_f(2\pi mkT/h^2)^{3/2}J]^N \exp(-U/RT) \quad (28)$$

where J is the partition function for the internal degrees of freedom of the molecule, m is the mass of the molecule, and h is Planck's constant. Other definitions of free volume have been proposed, but this one has the advantage that the free volume appears in the partition function as the effective volume in which the molecules move, it may be given a pictorial interpretation when the molecules are rigid, and it is simply related to the entropy. Eyring and his coworkers have developed the free volume description for the equation of state of liquids (5, 9, 13), and more recently Lennard-Jones and Devonshire (15, 16, 17) have started to use it in their description of dense gases. In terms of the free volume, the thermodynamical equation of state is

$$p = - \left(\frac{\partial U}{\partial V} \right)_T + RT \left(\frac{\partial}{\partial V} \log V_f \right)_T \quad (29)$$

Substituting our expression for U in terms of $B'(T)$ it follows that

$$\left(\frac{\partial \log V_f}{\partial V}\right)_T = \frac{1}{V} + \frac{f(V)}{V^3} + \frac{1}{V^2} \frac{d}{dT} (TB'(T)) \quad (30)$$

Integrating this expression with respect to volume and requiring that the free volume approach the true volume as the density becomes small, we obtain:

$$V_f = V \exp \left[\int \frac{f(v)}{V^3} dV - \frac{1}{V} \frac{d}{dT} (TB'(T)) \right] \quad (31)$$

The second term in the exponential corresponds to an increase in free volume with increasing temperature when the system is confined to a fixed amount of space. This shows that the model corresponding to the linearity of the internal energy with density is considerably more general than a gas of rigid spheres. This temperature dependence was missing in the free volume for gases proposed earlier by Hirschfelder, Stevenson, and Eyring (10). Another virtue of our free volume is that it leads to an increase in C_v with pressure, as shown by equation 24. Eyring and his coworkers (5, 9, 13) introduce a similar term in the specific heat, considering a temperature variation of b and supposing van der Waals' a to be independent of temperature.

The linearity of the internal energy with density is described most easily in terms of the Menke probability function. This function, $W(r)$, is defined as the number of molecules which lie within a unit of volume a distance r from a particular molecule divided by the average number of molecules lying in an arbitrary unit of volume. In terms of the probability function, the internal energy is

$$U = \frac{2\pi N^2}{V} \int_0^\infty W(r) E(r) r^2 dr + U_0(T) \quad (32)$$

If U is a linear function of $1/V$, it follows that $W(r)$ must be a function of r independent of volume, i.e., the same function for a dilute as for a dense gas. For the dilute gas,

$$W(r) = \exp(-E(r)/kT)$$

For liquids, the probability function has been determined from x-ray diffraction data for mercury (18), carbon tetrachloride (18), gallium (18), water (11), and for a few comparatively complicated substances, but as far as we were able to ascertain, it has never been determined for helium, hydrogen, neon, nitrogen, or argon, which are the substances for which we know $E(r)$. Figure 8 shows $W(r)$ for a dilute gas and its likely appearance for the case of a "normal" liquid or a dense gas. In the examples where the linear relationship holds, we should expect that the first maximum in $W(r)$ is the same for the dilute gas as for the liquid or dense gas, since this

part of the probability function depends on the actual collisions between a pair of molecules and is not greatly affected by the presence of neighbors. The two curves should differ in the relatively unimportant second and third maxima. From this standpoint, it follows that $W(r)$ cannot be exactly independent of volume, but this assumption may represent a good first approximation.

The deviations of the internal energy of gases and liquids from the linearity with density might be used to study the structure of these substances. As long as a change in the density produces only a change in the frequency but not a change in the character of molecular collisions, $W(r)$ is independent of volume. However, as the system becomes more and more dense the molecules will become geometrically constrained to move in a more or less regular lattice. Under these conditions $W(r)$

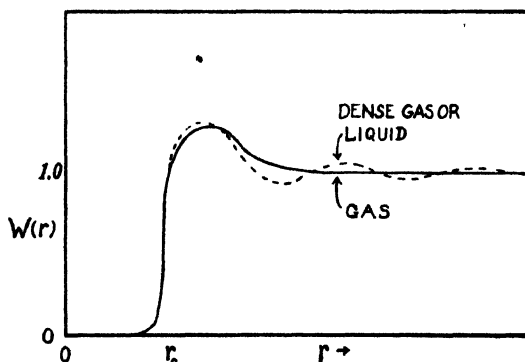


FIG. 8. $W(r)$ for a dilute gas and its likely appearance for the case of a "normal" liquid or a dense gas

will vary with the density of the system in something like the following manner:

$$W(r) = g(r)/V - h(r)/V^n \quad (33)$$

where $g(r)$ and $h(r)$ are independent of volume, and have maxima corresponding to the lattice points. For these dense systems it is clear that the lattice structure will set in, and the deviations of the internal energy from the linearity will occur in the neighborhood of the density of the crystal. It is in this region that we should like the correction factor for the internal energy (corresponding to $a/2V$ in the Beattie-Bridgeman equation) to be large.

SUMMARY

1. Any good equation of state for gases may be used to estimate the energy of interaction and collision diameter of molecules. The Beattie-Bridgeman equation is excellent for this purpose.

2. The Joule-Thomson coefficients extrapolated to zero pressure lead to an alternative method of determining these molecular constants which has some advantages.

3. Experimentally it is found that at high temperatures the internal energy of a gas at constant temperature is a linear function of the density. This leads to a simple equation of state which holds up to pressures of the order of 3000 atm. For such high pressures the Beattie-Bridgeman equation does not hold when the usual values of the constants are employed.

4. The linearity of the internal energy with density at constant pressure is explained in terms of the Menke probability function. Deviations from this law in the neighborhood of the critical temperature are due primarily to fluctuations.

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REFERENCES

- (1) BEATTIE, J. A., AND BRIDGEMAN, O. C.: *J. Am. Chem. Soc.* **49**, 1665 (1927).
- (2) BEATTIE, J. A., AND BRIDGEMAN, O. C.: *J. Am. Chem. Soc.* **50**, 3133 (1928).
- (3) BEATTIE, J. A., AND BRIDGEMAN, O. C.: *J. Am. Chem. Soc.* **50**, 3153 (1938).
- (4) BEATTIE, J. A., AND BRIDGEMAN, O. C.: *Z. Physik* **62**, 95 (1930).
- (5) EYRING, H., AND HIRSCHFELDER, J.: *J. Phys. Chem.* **41**, 249 (1937).
- (6) FOWLER, R. H.: *Statistical Mechanics*, 2nd edition. University Press, Cambridge (1936).
- (7) HAPPEL, H.: *Ann. Physik* **30**, 246 (1906).
- (8) HILDEBRAND, JOEL H.: *Solubility of Non-electrolytes*, American Chemical Society Monograph. Reinhold Publishing Corporation, New York (1936).
- (9) HIRSCHFELDER, J., EWELL, R. B., AND ROEBUCK, J. R.: *J. Chem. Phys.* **6**, 205 (1938).
- (10) HIRSCHFELDER, J., STEVENSON, D., AND EYRING, H.: *J. Chem. Phys.* **5**, 896 (1937).
- (11) KATZOFF, S.: *J. Chem. Phys.* **2**, 841 (1934).
- (12) KEENAN, J. H., AND KEYES, F. G.: *Thermodynamical Properties of Steam*. John Wiley and Sons, Inc., New York (1936).
- (13) KINCAID, J., AND EYRING, H.: *J. Chem. Phys.* **5**, 587 (1937).
- (14) LENNARD-JONES, J. E.: *Interatomic Forces*, Chap. X in *Statistical Mechanics* (reference 6).
- (15) LENNARD-JONES, J. E.: *Physica* **4**, 10, 941 (1937).
- (16) LENNARD-JONES, J. E., AND DEVONSHIRE, A. F.: *Proc. Roy. Soc. (London)* **A163**, 53 (1937).
- (17) LENNARD-JONES, J. E., AND DEVONSHIRE, A. F.: *Proc. Roy. Soc. (London)* **A165**, 1 (1938).
- (18) MENKE, H.: *Physik. Z.* **33**, 593 (1932).
- (19) MICHELS, A., BIJL, A., AND MICHELS, C.: *Proc. Roy. Soc. (London)* **A160**, 376 (1937).

- (20) MICHELS, A., AND MICHELS, C.: Proc. Roy. Soc. (London) **A160**, 348 (1937).
- (21) ROEBUCK, J. R.: Proc. Am. Acad. Arts Sci. **64**, 287 (1930).
- (22) ROEBUCK, J. R., AND OSTERBERG, H.: Phys. Rev. **46**, 785 (1934).
- (23) ROEBUCK, J. R., AND OSTERBERG, H.: Phys. Rev. **48**, 450 (1935).
- (24) ROEBUCK, J. R., AND OSTERBERG, H.: J. Am. Chem. Soc. **60**, 341 (1938).
- (25) SAGE, B. H., WEBSTER, D. C., AND LACEY, W. N.: Ind. Eng. Chem. **29**, 1188 (1937).
- (26) TRAUTZ, M., AND ADER, H.: Z. Physik **89**, 1 (1934).
- (27) URSELL, H. D.: Proc. Cambridge Phil. Soc. **23**, 685 (1927).

THE LIQUID STATE¹

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INTRODUCTION

The van der Waals centenary number of *Physica* (16) and the recent symposium of the Faraday Society on liquids (18) present many of the recent advances in this field. Since the whole thermodynamic theory of matter can be calculated from explicit partition functions, it is a problem of great interest to find such functions for liquids by every means at our disposal. The liquid must be quite similar to the solid at the melting point and similar to the vapor at the critical point, so that we require a function which approximates the Debye partition function for the solid near the melting point and passes continuously over into a form which will yield the van der Waals equation of state for gases. We now consider a particular case.

THE APPLICATION OF A VAN DER WAALS TYPE OF EQUATION TO DENSE LIQUIDS

In a previous paper (14) a number of kinetic theory equations for gases were modified in such a way as to make them applicable to liquids. In this section we extend the program started there by examining the conditions necessary for an equation of the van der Waals type to be valid over the entire range of volumes from the dilute gas to the dense liquid. It is well known that the van der Waals equation itself has a range of applicability only slightly greater than that of the ideal gas law, and that it fails badly even at volumes as great as that at the critical point.

There are two principal causes for deviations from the simple van der Waals equation. The excluded volume b can be taken to be equal to four times the volume of the molecules only at low gas pressures. As the gas

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is compressed, overlapping becomes important and must be corrected for. This problem has been considered by a number of people, including Happel (9), Majumdar (15), and Hirshfelder, Stevenson, and Eyring (10). These authors give an equation for the free volume V_f of the form:

$$V_f = V \exp[-(b/v) - \alpha_1(b/v)^2 - \alpha_2(b/v)^3 \dots] \quad (1)$$

where α_1 , α_2 , etc. are parameters. Another cause for deviations becoming important at volumes much smaller than the point at which overlapping becomes important is the repulsive force that the molecules exert on one another as they condense to form a close-packed liquid. In addition to these two effects, the temperature dependence of the effective volume of the atoms causes a significant decrease in van der Waals b as the temperature is increased.

Mercury was chosen as a test liquid for an equation of state corrected for these effects, because it provides an extreme example of a close-packed liquid and because all the necessary data have already been summarized (13). In setting up the partition function the static energy E_s is defined (as before (13)) as the potential energy that the liquid would have if the atoms remained fixed in their equilibrium positions. The form that we choose for E_s is:

$$E_s = -a/V + d \exp(-cV^{1/3}) \quad (2)$$

Here a/V and $d \exp(-cV^{1/3})$ represent the attractive and repulsive portions, respectively, of the static energy. The three parameters a , d , and c were very simply evaluated from three properties of the liquid at the absolute zero. The ones selected were the energy of vaporization, which is equal to the value of E_s at $T = 0$, the volume which coincides with the minimum in E_s , and the compressibility which is given in terms of the second derivative.² The simultaneous equations to be solved are:

$$a/V - d \exp(-cV^{1/3}) = \Delta E_{\text{vap.}} = 63.18 \times 10^{10} \text{ ergs per mole} \quad (3)$$

$$a/V^{4/3} - (dc/3) \exp(-cV^{1/3}) = 0 \quad (4)$$

and

$$dV/dP = V^{4/3}[4a/3V^{5/3} - (c^2d/9) \exp(-cV^{1/3})]^{-1} = -38.2 \times 10^{-12} \text{ absolute units} \quad (5)$$

These equations may be readily reduced to two linear equations and a quadratic, to yield the expression for E_s :

$$E_s = -10.069 \times 10^{12}/V + 8.560 \times 10^{21} \exp(-10.50V^{1/3}) \text{ ergs per mole} \quad (6)$$

² No absolute significance is attached to the properties of the liquid at the absolute zero. The extrapolated properties at $T = 0$ are regarded merely as those which the liquid would have if it continued to behave at temperatures below the melting point as it does at temperatures above it.

The volume at $T = 0$ was taken as 14.05 cc. The particular value of 63.18×10^{10} ergs per mole for $\Delta E_{\text{vap.}}$ was chosen at $T = 0$, because it gives the correct entropy of the liquid at its melting point and thus the correct entropy of fusion. This value for $\Delta E_{\text{vap.}}$ ($T = 0$) is very close to what one obtains by extrapolation of the best thermal measurements (12).

If the equation is to be employed at temperatures other than $T = 0$, some form must be chosen for the free volume. Although the form that has been previously employed by us (13) is satisfactory for the close-packed liquid, it fails to extrapolate smoothly to yield the ideal gas expression at large volumes. Equation 1, an expansion in powers of (b/V) , appears promising, but it is a rather clumsy expression with which to work. A much simpler expression, which we have found to be more satisfactory, is

$$V_f = V \exp[-(b/V)^n] \quad (7)$$

in which the sum of powers of b/V has been replaced by a single term raised to an arbitrary power.

Using equation 7 the partition function becomes

$$f = [(2\pi mkT)^{3/2}/h^3]V \exp[-(b/V)^n] \exp(-E_s/RT) \quad (8)$$

and the equation of state follows from equation 8 by the conventional method.

$$P = RT (\partial \ln f / \partial V)_T = -a/V^2 + (dc/3V^{2/3}) \exp(-cV^{1/3}) + (RT/V)[1 + n(b/V)^n] \quad (9)$$

Since the parameters in E_s have already been determined, the unknown in equation 9 at any particular temperature is the quantity $n(b/V)^n$. This was determined at the melting point and at the boiling point from the experimental vapor pressures. This left as the only unknown the value of n , which was found to be 1.30 from equation 9, utilizing the experimental volume of the liquid at its melting point. These data give b equal to 60.67 and 50.07 cc. at the melting point and at the boiling point, respectively. Values of b at other temperatures were computed from the relation:

$$b = (119.05 - 10.70 \ln T) \text{ cc.} \quad (10)$$

The agreement of the calculations with the observed data is shown in table 1. The six observations that were used to determine the six constants of the partition function are given in parentheses. The compressibilities quoted are from Hubbard and Loomis (11), and the other data are the same as those previously employed (13). In comparing the calculations with the observations it should be recalled that it has been our aim throughout to make the partition function as simple as possible,

TABLE I
A comparison of the observed properties of liquid mercury with those computed from the partition function

TEMPERATURE	VOLUME		VAPOUR PRESSURE		C_p		C_v		$\beta \left(\equiv - (1/V) (\partial V / \partial P)_T \right)$		ENTROPY	
	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
$^{\circ}\text{K.}$	cc.	cc.	mm.	mm.	cal. per mole per degree	cal. per mole per degree	cal. per mole per degree	cal. per mole per degree	(dynes per cm. ²) ⁻¹	(dynes per cm. ²) ⁻¹	E.U.	E.U.
0	14.050	(14.050)										
234 (m.p.)	14.65	(14.66)										
273	14.76	14.75	1.99×10^{-6}	(1.99×10^{-6})	6.79	6.58	6.06	6.02		27.2×10^{-13}	16.70	(16.70)
373	15.03	15.01	1.88×10^{-4}	1.86×10^{-4}	6.72	6.60	5.91	5.97	39.2	42.0		
473	15.30	15.27	0.269	0.266	6.60	6.67	5.61	5.86	44.1	48.6		
573	15.58	15.56	17.0	16.8	6.60	6.76	5.46	5.77		56.6		
630 (b.p.)	15.75	15.74	245.4	242.7	6.67	6.85	5.33	5.67		66.8		
			760	(760)	6.72	7.02	5.28	5.62		73.7		

and to evaluate the parameters in the easiest possible manner. By employing a more laborious method of securing the parameters it would no doubt be possible to obtain a better partition function.

Inspection of equation 9 reveals that at large volumes it reduces to the ideal gas law, $PV = RT$. Whether it gives satisfactory results at intermediate volumes is, however, still to be determined. Although no extensive PV data are available for liquid mercury except at temperatures below the boiling point, the critical temperature and pressure have been determined by Birch (2), who has also estimated the critical volume from the data of Bender (1; see also 20). From the conditions that $(\partial P/\partial V)_T$ and $(\partial^2 P/\partial V^2)_T$ equal 0 at the critical point we have the following simultaneous equations to be solved for T_c , V_c , and P_c :

$$P + a/V^2 = (RT/V)[1 + n(b/V)^n] \quad (11)$$

$$2a/V^2 = (RT/V)[1 + (n + n^2)(b/V)^n]$$

$$6a/V^2 = (RT/V)[2 + (2n + 3n^2 + n^3)(b/V)^n]$$

The repulsive contribution to E_s has been omitted from these equations, since it can be neglected at such large volumes.

The calculated values are compared with those experimentally determined in table 2. The calculated pressure is given only approximately, because it is extremely sensitive to the extrapolated value of b . The success of the partition function in predicting approximately the right critical constants is of considerable interest, since the bonding in metallic solids and liquids is usually thought of as quite different from the van der Waals forces acting between pairs of molecules. Unfortunately, mercury is the only liquid metal for which the data are available for setting up a partition function of this kind.

We now proceed to certain general considerations.

Partition functions

For temperatures several times the Debye characteristic temperatures, $\theta(= h\nu'/k)$, the Debye solid partition function approaches the Einstein form:

$$K = \left(1 - \exp\left(-\frac{h\nu}{kT}\right)\right)^{-3N} \exp\left(\frac{E}{kT}\right) (f_r f_i)^N \quad (12)$$

At still higher temperatures K takes the classical form:

$$K = \left[\frac{kT}{h\nu}\right]^{3N} \exp\left(\frac{E}{kT}\right) (f_r f_i)^N \quad (13)$$

Here N , ν' , ν , and E are the number of molecules, the maximum frequency, the mean frequency ($\nu = 3/4 \nu'$), and the energy of vaporization

for N molecules at the absolute zero, respectively. E is usually expressible as a function of volume alone, unless important structural changes occur; k , h , and T are the Boltzmann constant, Planck's constant, and the absolute temperature, respectively. f_r and f_i are the partition functions for the rotational and internal degrees of freedom of a molecule.

The partition function which leads to van der Waals equation is:

$$\begin{aligned} f_o^N/N! &= \left(\left(\frac{(2\pi mkT)^{3/2}}{h^3} (V-b) \right)^N \exp\left(\frac{a}{VbT}\right) \right) \frac{1}{N!} (f_r f_i)^N \\ &= \left[\frac{(2\pi mkT)^{3/2}}{h^3} \frac{(V-b)}{N} \right]^N e(f_r f_i)^N \exp\left(\frac{a}{VbT}\right) \end{aligned} \quad (14)$$

(We have used the Sterling approximation $N! = N^N e^{-N}$.) Here m , V , $(V-b)$, a/v , and e are the mass of the molecule, the volume occupied by N molecules, the free volume occupied by N molecules, the potential energy, and the base of the natural system of logarithms, respectively. If we identify the two energies and also the terms in square brackets in

TABLE 2
Critical constants for mercury

TEMPERATURE		VOLUME		PRESSURE	
Observed	Calculated	Observed	Calculated	Observed	Calculated
°K.	°K.	cc.	cc.	dynes per cm. ²	dynes per cm. ²
1730	1500	about 40	37.5	1600×10^6	about 1000×10^6

equations 13 and 14, we see that the gas partition function has an extra factor e , which corresponds to the communal entropy (6, 10, 13) $R = R \ln e$. Our reasons for believing that most of the communal entropy enters at the melting point will be given later. For a liquid with communal sharing in the region where classical mechanics applies we thus expect the following expression to be satisfactory:

$$f_o^N/N! = \left(\frac{(2\pi mkT)^{3/2}}{h^3} \frac{V_f}{N} \right)^N e(f_r f_i)^N \exp\left(\frac{E}{kT}\right) \quad (15)$$

V_f is now the free volume for N molecules, and the explicit forms to be taken by V_f , E , and f_r are questions to be answered in a theory of liquids.

Melting and the communal entropy

At the melting point we have the relation

$$A_l + pV_l = A_s + pV_s. \quad (16)$$

where the subscript l indicates the liquid and s indicates the solid. Also

$$A_l = -kT \ln f_l^N/N! \quad (17)$$

and $A_s = -kT \ln K$ (13). From thermodynamics the pressure satisfies the well-known equation

$$p = - \left(\frac{\partial A}{\partial V} \right)_T \quad (18)$$

If $A_l + pV_l > A_s + pV_s$, the solid is stable, while for the reverse inequality the liquid is stable. If, for a given temperature, A_s be plotted as ordinate with the volume as abscissa, then using equation 8 we see that the intersection of the tangent to the curve with the ordinate $V = 0$ gives the Gibbs free energy for the solid at the temperature and volume corresponding to the point of tangency, the pressure of course being the negative of the slope. Plotting the Helmholtz free energy for the liquid and gas the same procedure gives their Gibbs free energy as a function of

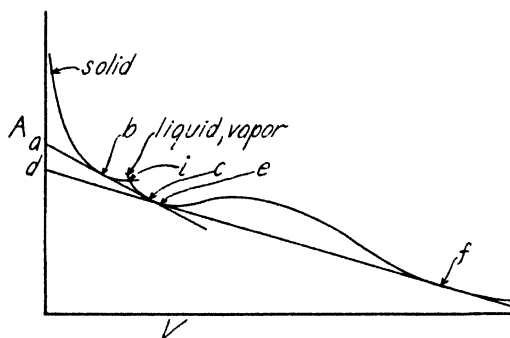


FIG. 1. The Helmholtz free energy A for liquid, gas, and solid at some temperature T is plotted against the volume as abscissa. The intercept a gives the Gibbs free energy for liquid and solid in equilibrium at the pressure given by the negative of the slope of the line ab . The corresponding volumes for solid and liquid are the abscissas of the points b and c , respectively. The line def has a corresponding significance for the liquid-vapor equilibrium

V , T , and P . The common tangent to the A curves of two phases fixes the pressure and the two volumes at which the two phases are in equilibrium at that particular temperature. For the triple point there is of course a common tangent to all three phases. This procedure is discussed at length in treatments like the one by Kohnstamm (17) in the *Handbuch der Physik*. The situation for a solid and liquid which expands upon melting is indicated in figure 1. Clearly an explicit form for the partition functions for the solid and liquid phases constitutes a theory of melting.

Only those points on the A curves are thermodynamically stable for which the tangent fails to intersect any other section of these curves. The A curve for the solid differs from that for the liquid-vapor because of some change in structure, having as a result the instability of volumes

intermediate between those for the points *b* and *c*. Since the potential energy at such intermolecular distances, for molecules held by van der Waals forces, almost certainly increases with distance in spite of any structural change, the stabilization of the liquid arises from a sudden increase of entropy with volume. For complex molecules there will be increases in the entropy of rotation when neighbors get farther apart during melting, but this is only incidental to the increase in entropy associated with translational degrees of freedom. Most monatomic molecules melt with an increase of about two entropy units at atmospheric pressure (10). This is the value to be expected if the communal entropy is attained, principally during the process of melting. Rice (17) argues that, because the entropy of melting for monatomic molecules such as argon drops with the pressure below two units, probably the communal entropy is of minor importance on melting. This is of course evidence that the entire two units do not necessarily come in at the melting point, but this was already clear for another reason, i.e., the values for sodium and potassium are slightly less than two units even at atmospheric pressure.

We have an analogous case in the process of vaporization. Thus the term $p(V_g - V_l)$ contributes RT to the energy and R to the entropy of vaporization at low pressures, but both values drop to zero at the critical point. V_g and V_l are the molal volumes of liquid and vapor, respectively.

Gurney and Mott (8) have given the curve for the communal entropy as a function of the number of molecules, n , in each of N/n groups which communally share volume, it being understood that the N/n groups do not share communally with each other. The corresponding Helmholtz free energy is:

$$A = -kT \ln \left\{ \left(\frac{(2\pi mkT)^{3/2}}{h^3} f_i f_j \exp \left(\frac{E}{kT} \right) \right)^N \left[\left(\frac{nV_f}{N} \right)^n \frac{1}{n!} \right]^{N/n} \right\} \quad (19)$$

and the communal entropy per mole is:

$$S(n) = R \left(\log n - \frac{1}{n} \log n! \right) \quad (20)$$

where $S(1) = 0$; $S(5) = 0.66R$; $S(27) = 0.9R$; $S(\infty) = R$.

Now the condition that there shall be local communal sharing of free volume must be that the local density drop sufficiently to permit the structure to collapse freely in the various directions. If the molecules were points we would of course have communal sharing of volume. Thus the lack of communal sharing arises from the finite dimensions of the molecules, i.e., from their interlocking. Tonks (19), of course, finds communal sharing among molecules arranged in a linear filament. Thus if molecules were arranged in a simple cubic lattice, each of the linear

filaments parallel to any one of the three axes would show communal sharing, so that from equation 20 we see that the system would possess practically the full entropy R . However, even in the liquid state the system has not expanded to the point where filaments slide by other filaments with ease, as is shown by the considerable activation energy for viscous flow. Viscosity of course measures the ease with which layers of molecules slide by each other (4, 5). Thus communal sharing (which measures the ease of collapse of the structure) and fluidity or diffusion (which presumably measure the ease of rotation of double molecules (10)) are only slightly different aspects of the same problem of the degree of correlation between the motion of neighbors, and we regard the great change of fluidity upon melting as compelling evidence for a corresponding great change in the communal entropy.

The correlation between the motion of neighbors is of course a strong function of the volume, and this can be expressed in some such form as the following expression for A :

$$A = -kT \ln \left\{ \left(\frac{(2\pi mkT)^{3/2}}{h^3} f, f, \exp \left(\frac{E}{kT} \right) \frac{V_f}{N} \right)^n \cdot \sum_{n=1}^{\infty} \exp \left(\frac{S(n+1) - S(n)}{k} - \frac{(E(n+1) - E(n))}{kT} \right) \right\} \quad (21)$$

Here $S(n)$ is defined by equation 20 and E_n is the energy required to expand N/n regions, each containing n molecules, from the average volume up to that critical volume at which communal sharing begins. We have not yet tested explicit forms of equation 21 in efforts to explain the change of the melting point with pressure, but a knowledge of the activation energy for viscous flow should be of assistance in estimating $E(n)$ and in checking intuitive estimates of what the critical volumes for sharing should be. We now consider briefly methods of estimating the free volume.

The free volume

In a recent paper (14) we have considered at length possible ways of calculating the free volume. In this paper we have seen that $V \exp - \left(\frac{b}{v} \right)^n$ gives a satisfactory expression for this quantity for mercury, and we now wish to discuss briefly the velocity of sound method (14). The basic idea is that the time used by the sound wave in travelling through the atoms themselves is negligible compared with that used in traversing the free volume, where the wave is carried by the atoms moving with the velocity of sound in the gas. This yields the equation

$$u_l = u_g \left(\frac{V}{V_f} \right)^{1/3} = \left(\frac{kT\gamma}{m} \right)^{1/2} \left(\frac{V}{V_f} \right)^{1/2} \quad (22)$$

where u_l , u_g , m , V , and V_f are the velocity of sound in the liquid, the velocity in the gas, the weight of a molecule, the molal volume, and the molal free volume of the liquid, respectively. If for the moment we neglect communal sharing, we obtain for the partition function for one translational degree of freedom in the liquid:

$$\begin{aligned} \frac{(2\pi mkT)^{1/2} (V_f/N)^{1/3}}{h} &= \frac{(2\pi mkT)^{1/2}}{h} \left(\frac{kT\gamma}{m}\right)^{1/2} \left(\frac{V}{N}\right)^{1/3} \frac{1}{u_l} \\ &= \frac{(\gamma 2\pi)^{1/2}}{u_l} \frac{kT}{h} \left(\frac{V}{N}\right)^{1/3} = 2.51 \left(\frac{V}{N}\right)^{1/3} \frac{kT}{h} \frac{\gamma}{u_l} \end{aligned} \quad (23)$$

Now at high temperatures compared with the characteristic temperature

$$\theta = \frac{h\nu'}{k} = \frac{h}{k} \left(\frac{9N}{4\pi V}\right)^{1/3} u_s$$

the Debye theory (7) for solids yields the limiting partition function:

$$\frac{kT}{h\nu} = \frac{4}{3} \frac{kT}{h\nu'} = \frac{4}{3} \left(\frac{4\pi V}{9N}\right)^{1/3} \frac{kT}{hu_s} = 1.5 \left(\frac{V}{N}\right)^{1/3} \frac{kT}{hu_s} \quad (24)$$

Here u_s is the velocity of sound in the solid. Thus we see that our very simple model for the free volume of a liquid leads to formally the same translational partition function as the Debye theory for the solid. The free volume calculated from equation 22 is in satisfactory agreement with that found by other methods (14). However, it is possible that improvements in our model and examination of additional data will lead to the adoption of a proportionality constant in equation 23 more nearly equal to that in equation 24.

Brillouin (3) has treated liquids in a manner analogous to Debye's solid treatment and has obtained interesting results. When the activation energy for viscous flow disappears, as it does in the neighborhood of the critical point, the liquid loses its ability to store the potential energy resulting from shearing stresses. Thus transverse sound waves only involve kinetic energy. In this way Brillouin explains why the translational specific heat drops from about 6 cal. near the melting point to about 4 at the critical point. Our velocity of sound method provides an alternative approach to these questions.

REFERENCES

- (1) BENDER: *Physik. Z.* **16**, 246 (1915); **19**, 410 (1918).
- (2) BIRCH, FRANCIS: *Phys. Rev.* **41**, 641 (1932).
- (3) BRILLOUIN: *Trans. Faraday Soc.* **33**, 54 (1937).
- (4) EWELL AND EYRING: *J. Chem. Phys.* **5**, 726 (1937).
- (5) EYRING: *J. Chem. Phys.* **4**, 283 (1936).
- (6) EYRING AND HIRSCHFELDER: *J. Phys. Chem.* **41**, 249 (1937).
- (7) FOWLER: *Statistical Mechanics*, p. 127. University Press, Cambridge (1936).

- (8) GURNEY AND MOTT: J. Chem. Phys. **6**, 222 (1938).
- (9) HAPPEL, H.: Ann. Physik **4**, 21, 342 (1906).
- (10) HIRSCHFELDER, STEVENSON, AND EYRING: J. Chem. Phys. **5**, 896 (1937).
- (11) HUBBARD AND LOOMIS: Phil. Mag. [7] **5**, 1177 (1928).
- (12) KELLEY, K. K.: U. S. Bur. Mines, Bull. 393 (1936).
- (13) KINCAID AND EYRING: J. Chem. Phys. **5**, 587 (1937).
- (14) KINCAID AND EYRING: J. Chem. Phys. **6**, 620 (1938).
- (15) MAJUMDAR, R.: Bull. Calcutta Math. Soc. **21**, 107 (1929).
- (16) Physica **4**, No. 10 (1937).
- (17) RICE, O. K.: J. Chem. Phys. **5**, 476 (1938).
- (18) SYMPOSIUM ON LIQUIDS: Trans. Faraday Soc. **33**, 1-282 (1937).
- (19) TONKS, LEWI: Phys. Rev. **50**, 955 (1936).
- (20) WEBER: Commun. Kamerlingh Onnes Lab. Univ. Leiden, Suppl. No. **43** to Nos. **145-156**, p. 23 (1920).

THE STATE OF LIQUID HELIUM NEAR ABSOLUTE ZERO¹

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I. INTRODUCTION: STATIC EQUILIBRIUM AND QUANTUM-MECHANICAL UNCERTAINTY

It is customary to believe that space lattice structures represent the most stable configurations of force centers, as is illustrated by the well-known arrangements of molecules or atoms. Indeed, the configuration of minimum of potential energy of such force centers is always given by a certain lattice type. Thus for molecules of spherical symmetry a closest-packed structure (cubic or hexagonal) represents the minimum of potential energy. *If the kinetic energy is sufficiently small*, i.e., for sufficiently low temperatures, it is usual to suppose that such a lattice structure will be realized. General principles of thermodynamics also require that a certain state of order should be established, when a system of many equivalent particles approaches absolute zero. Thus it seems quite appropriate to identify the lattice order of the solid state with that order which, for low temperatures, is required by the third law of thermodynamics.

This argument, however, is not entirely conclusive. According to quantum mechanics the *kinetic energy of a particle can never be exactly zero* if, at the same time, the space coördinates are restricted to a certain finite region. This would contradict the uncertainty relation. A certain "zero point motion" will remain. Thus it is well known that the electrons in the interior of the atoms, as well as the particles constituting the nuclei, by no means assume configurations of geometric symmetry (polyhedra, etc.), such as were sometimes proposed in the early stages of atomic or nuclear physics, when it was thought necessary to search for configurations of minimum *potential energy*. The statistical distribution realized by the lowest quantum state rather represents a compromise between the mini-

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imum of potential *and* of kinetic energy. It is to be regarded as the minimum of the sum of both so that the uncertainty relation $\Delta q \cdot \Delta p \geq \frac{h}{4\pi}$ is simultaneously fulfilled. It depends entirely on the order of magnitude of the actual interaction forces and of the masses whether, in this compromise, the minimum of total energy is realized with a very small Δq or with a Δq large compared with the mean distance of the particles. It is only in the case where Δq is smaller than the mean distance of the particles that their locations may still reproduce, to some extent, the positions of the minima of the potential energy.

In general, the occurrence of "*quantum structures*", is considered to be restricted to *subatomic* dimensions ($\lesssim 10^{-8}$ cm.). A simple estimate explains this fact. The kinetic "zero point energy", E_0 , of a particle of mass M , the center of gravity of which is confined to the interior of a sphere of radius R , is given by

$$E_0 = \frac{h^2}{8MR^2} \quad (1)$$

For electrons in Coulomb fields ($\sim e^2/R$), E_0 becomes comparable to, or greater than, the potential energy for values of $R \sim \frac{h^2}{8Me^2} \sim 3 \times 10^{-8}$ cm. Accordingly for nuclear particles with a mass which is about 2000 times greater, the limit for the appearance of quantum structures is $\sim 10^{-11}$ cm. From this one can conclude that for atoms or molecules which have the same or greater mass than the atomic nuclei, and for localizations in regions of the size of atomic distances ($\sim 10^{-8}$ cm.), one is far from such quantum effects. If we express E_0 in calories per mole and M by the molecular weight and assume $R = 10^{-8}$ cm, we obtain

$$E_0 = \frac{473}{M} \text{ (cal. per mole)} \quad (1')$$

Usually this is very small compared to the contribution of the potential energy, as the latter generally provides potential holes of some thousands of calories per mole. This fact explains why quantum mechanics is practically confined to the subatomic world, and why the motion and localization of atoms or molecules in their mutual force fields can, to a very good approximation, be treated by means of classical mechanics. These calculations may be refined by adding some subsequent quantum corrections, but in general these quantum effects are only small quantitative supplements and have no fundamental significance for the arrangement or motion of the atoms.

II. THE VAN DER WAALS FIELD OF HELIUM

There is, however, the somewhat exceptional case of liquid helium, which seems to present the peculiar example of a *quantum structure of*

macroscopic dimensions, and which manifests a variety of highly enigmatic phenomena. Helium is the only substance that cannot be transformed into the solid state merely by cooling. Actually it has in its liquid state, at 2.19° A., a thermal anomaly, the so-called λ -point (11, 12). At this temperature its specific heat shows a discontinuity and most of its properties change abruptly. In particular the heat conductivity (13, 22, 3, 15) and the fluidity (28, 4, 5, 2, 6, 10, 17) increase enormously when one cools helium below the λ -point. Thus one speaks of superheatconductivity and of superfluidity in this modification of liquid helium (called helium II).

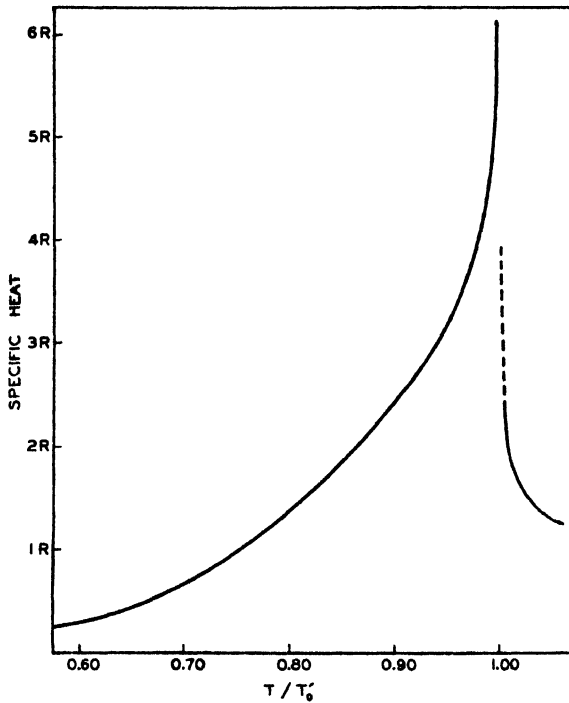


FIG. 1. Specific heat of liquid helium, according to W. H. Keesom and H. P. Keesom (13)

It is only under pressure that solid helium can exist; extrapolated to the absolute zero this pressure amounts to about 25 atm. Below the λ -point the entropy difference between the liquid and the solid phase decreases rapidly toward zero with falling temperature, which indicates that the liquid phase goes into a peculiar state of order. This change towards an ordered state begins at the λ -point and occurs continuously in a relatively small temperature range. It would be interesting to know what kind of order is realized in this liquid state.

How unusual the situation with helium is, will become evident if one

realizes that from equation 1' one would obtain a kinetic zero point energy of 118 cal. per mole, whereas the experimental total energy amounts to only about 14 cal. per mole.

As it is impossible to solve the quantum-mechanical many-body problem of N interacting helium atoms, even in any reasonable approximation, we prefer a sort of semi-empirical manner of discussion. The interaction forces between helium atoms are relatively well known. We will use the expression given by Slater and Kirkwood (24) for the energy of two helium atoms at a fixed distance r (in Å. units):

$$\varphi(r) = \left(77e^{-4.6r} - \frac{0.149}{r^6} \right) 10^{-11} \text{ erg} \quad (2)$$

This expression has been found to give a rather good agreement with experiment, when used to calculate the second virial coefficient of the gas equation. Thus it might perhaps be considered as more reliable than would be granted on the basis of the theoretical calculation alone.

All of the following discussion depends essentially on the fact that the actual molecular volume of liquid helium II is very much larger compared with what one would expect from the range of the helium forces. This peculiarity can be explained (23) as being caused by the contribution of the zero point energy, which increases very rapidly with increasing density and operates, therefore, like a kind of additional repulsive force.³ In a previous publication (18) I have given a quantitative estimate for this zero point energy by using equation 1 for the zero point energy at high densities, where any atom can be considered as confined to a spherical region formed by its nearest neighbors. For lower densities this formula had to be corrected, in order to account for the fact that in this case the "mean free path" is, of course, much longer than the shortest atomic distance.

In order to learn something about the most favorable coördination number of the atoms in the liquid state, let us localize them, provisionally, in the different configurations of regular lattices, taking the experimental molecular volume of liquid helium, which has been found to be about 27.6 cc. In figure 2 we have pictured schematically, for different regular lattices, the distribution of the neighbors of a given atom. The length of the vertical lines and the added numbers give the number of neighbors at the distances in question.

These vertical lines have been so arranged as to correspond to the abscissae of the potential curve given by equation 2. The ordinates of the potential curve have been chosen in such a way as to give the energy of a

³ This "zero point energy of mean free path" has nothing to do with the zero point energy of Fermi statistics. It comes from the finite cross section of the molecules; it exists as well for Bose as for Fermi statistics, but it disappears for point molecules.

pair of helium atoms multiplied by one-half of Avogadro's number. Thus we need simply to add the contributions of all the neighbors of one atom in order to get the total potential energy per molecular volume. At the right-hand side we have given the values of this total potential energy for different lattices.

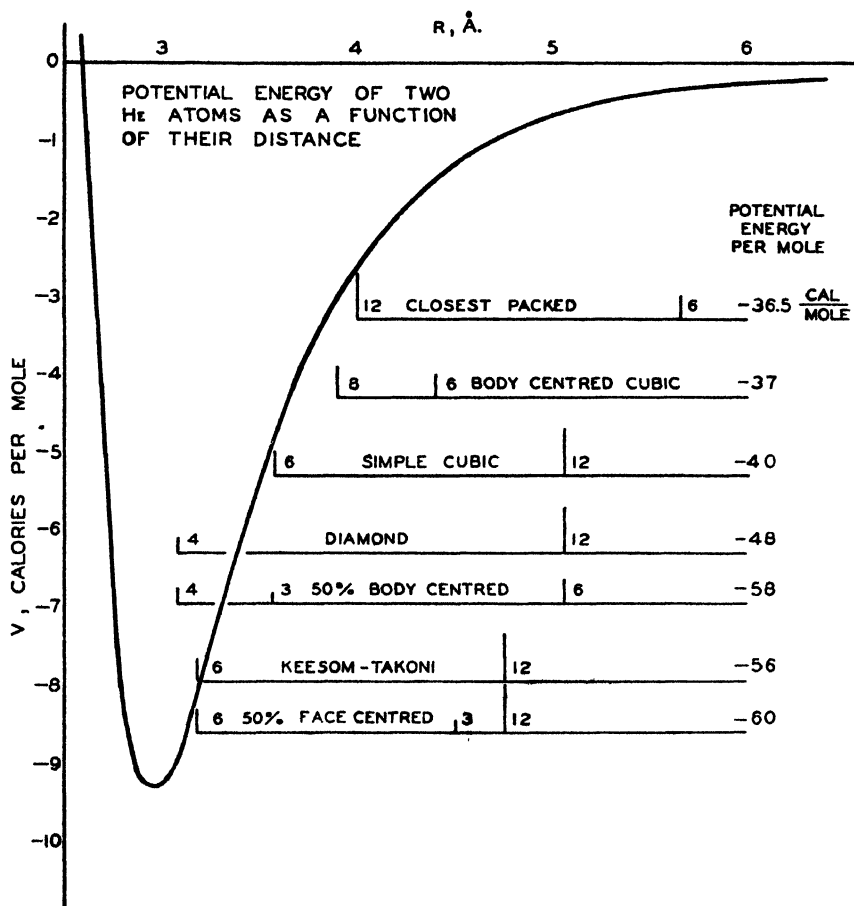


FIG. 2. Potential energy for different configurations of helium atoms

From this scheme one notices at once that, for the large molecular volume found experimentally, the closest-packed structure (coördination number 12) is by no means of particularly low energy. The coördination number 4, as realized in the diamond structure, would give a much better utilization of the available van der Waals field (48 cal. per mole instead of 36.5 cal. per mole). For this small density it is much more favorable for any atom to have four neighbors at a smaller distance than twelve at a greater one.

For the solid state, stable under a pressure of 25 atm. and of a molecular volume of 19.2 cc., the linear dimensions of the different lattices would have to be reduced by a factor

$$\sqrt[3]{\frac{19.2}{27.6}} = 0.89$$

and one reads from the figure that if the locations are contracted in this way, it would be the closest-packed structure which would give the best utilization of the actual forces.

From this it has been concluded (18) that helium in the liquid state might have a much smaller coördination number (presumably 4) than in the solid state (presumably 12).

It has also been emphasized (18) that it might be rather questionable whether one is entitled to go beyond this and to conclude that the helium atoms really assume the order of a diamond lattice. With regard to the presumably big zero point motion of the light helium atoms, one could, of course, only speak of an ultimate statistical preference for the vicinity of those lattice points. An estimate of the amplitude of this zero point motion may be obtained by means of equation 1. The kinetic zero point energy, E_0 , may be obtained semi-empirically as the difference of the observed total energy (-14 cal. per mole) minus the above calculated potential energy (-48 cal. per mole). This yields $E_0 = 34$ cal. per mole. From this and from equation 1 we obtain a sphere of radius

$$R = \sqrt{\frac{473}{4.34}} = 1.87 \text{ \AA.}$$

as the minimum range required for the zero point motion. In a diamond lattice of the density of liquid helium, the distance from a central atom to its four next neighbors is 3.09 \AA. However, owing to the repulsive forces, a closer approach than perhaps 2.4 \AA. is not possible, which means a free range of only 0.7 \AA. in this direction. The distance to the center of one of the confining tetrahedron surfaces amounts to 1.02 \AA. Hence there must be a considerable probability of finding the central atom outside of the tetrahedron of its neighbors. Even this, however, might not necessarily exclude the possibility that the immediate neighborhood of the diamond lattice points offers some statistical preference for the helium atoms.

Fröhlich took this point of view as a basis in order to explain the λ -phenomenon of helium (8). He noticed the following peculiarity of the diamond lattice (figure 3). While any atom is surrounded by a tetrahedron first neighbors, (e.g., A by the tetrahedron $B_1B_2B_3B_4$), there are, on the other hand, tetrahedra of the same size (e.g., $B_1B_4B_5B_6$) which are empty. These empty centers also form a diamond lattice of the same

dimensions as the original one. The two lattices taken together form a body-centered cubic lattice of $2N$ places for N atoms. According to Fröhlich the λ -phenomenon of liquid helium should be an order-disorder transition between the N holes and the N atoms in that body-centered cubic lattice of $2N$ places. The transition was treated along the lines of the Bragg-Williams-Bethe theory of order-disorder transitions in alloys, in close analogy to the transition observed with β -brass. Below the λ -point the helium atoms should show an increasing preference for one of the two diamond lattices, whereas above the λ -point the N atoms should be distributed at random over the $2N$ places.

This theory leads, in fact, to a discontinuity of the specific heat, and the amount of entropy corresponding to this ordering process has been found in satisfactory agreement with the experimental value.

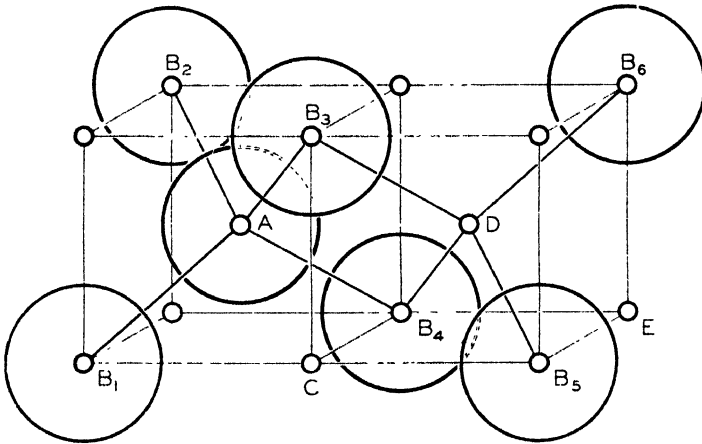


FIG. 3. Body-centered cubic lattice (small spheres) containing a diamond lattice (large spheres). The size of the large spheres has been taken to represent helium atoms as spheres of 2.5 \AA . diameter for a molecular volume of 27.6 cc

III. NON-STATIC EQUILIBRIUM

Though actually this explanation of the λ -phenomenon could not be maintained, it is quite instructive to learn why it failed (19). According to Fröhlich's idea a diamond lattice of helium atoms should, when partly formed, produce a molecular field so that any further helium atom shows a definite preference for becoming attached at those points which belong to the same diamond lattice, that is, the binding energy at a diamond point should be greater than anywhere else, in particular, greater than at the hole-points. It is, however, easy to see that, on the contrary, the binding energy right at a hole would be considerably greater than at a lattice point. It is true that these holes have four nearest neighbors at exactly the same

distance (3.09 \AA .) as the lattice points of the diamond lattice, but, in addition, they possess six second neighbors at an only slightly greater distance of 3.57 \AA ., which the diamond points do not possess (because at this distance, e.g., AD , there are the holes!). These second neighbors contribute considerably to the binding energy at the hole-points (about 50 per cent to the potential energy). Therefore no such coöperative phenomenon will appear as supposed by Fröhlich.

We may gather, however, some information from this model as to the actual distribution of the atoms at absolute zero. Suppose, at first, that all atoms, except one, be fixed in a diamond lattice. Let us further draw the potential energy curve of this one movable atom for different positions in the lattice. Figure 4 shows the shape of this potential field along the following broken path: from the original rest position (A) through the center

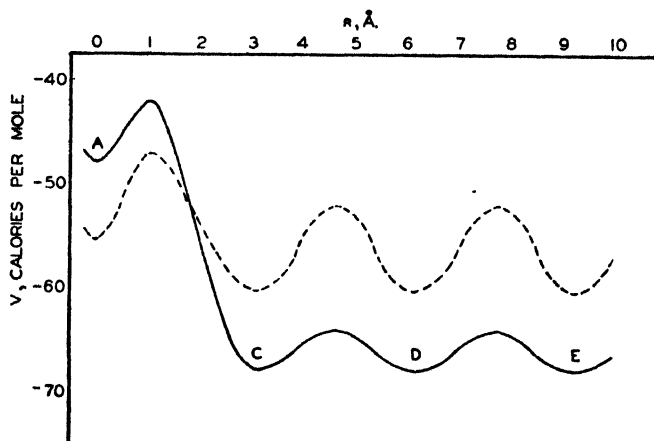


FIG. 4. Potential field in a diamond lattice

of one of the four adjacent tetrahedral surfaces, $B_1B_2B_3$, to the nearest hole (C), from C to the next hole (D), and then from any hole to the next hole. In its lowest quantum state the movable atom obviously will frequent particularly the holes C , D , etc., and since this occurs without preference for any of them, the atom will be, with equal probability, at each of these holes and practically never at its original position (A). It will not be hindered from circulating through the whole lattice, the potential barriers being very low. If now we liberate the fixed atoms successively, one after the other, they also will preferentially frequent the holes. However, if a fraction of the atoms has, in such a way, assumed the new distribution, it will be necessary to correct the potential function. With increasing occupation of the holes the binding energy will increase at the original diamond points and will decrease at the holes. (Compare

the dashed curve in figure 4.) One sees that finally, after all atoms are liberated, no distinction between one or the other of the diamond lattices will remain. All of the $2N$ places of the embracing *body-centered cubic lattice* will be equivalent, and each place will be occupied *with probability* one-half by a helium atom.

In this 50 per cent occupied configuration (see figure 2) every atom has, on the average, four nearest neighbors at a distance of 3.09 \AA ., exactly as in the diamond lattice, but, in addition, there are on the average three second neighbors at the distance of 3.57 \AA .. In the diamond lattice proper there are twelve second neighbors at a distance of 5.04 \AA ., whereas in the 50 per cent occupied centered lattice there are, at this distance, on the average only six atoms. However, at this great distance the influence of the van der Waals forces is almost negligible. In all, the gain of potential energy in favor of the 50 per cent occupied lattice would amount to about 10 cal. per mole. In addition the kinetic zero point energy of the new configuration would also be lower, as now each atom has on the average two locations; it has, so to speak, twice as much volume at its disposal as in the ordinary diamond lattice.

This method of discussion can of course not claim to give even an approximate basis for the definite distribution of helium atoms at absolute zero. It should rather be regarded as an indirect demonstration of the fact that, in any case, *the most stable configuration of the helium atoms can not be represented by any ordinary simple static space lattice*. In such manner are we led to visualize non-static equilibrium configurations.

With regard to regular lattices with $2N$ places for N atoms, we may remark that the body-centered lattice is by no means distinguished by particular stability. A *face-centered lattice of $2N$ places*, each equally occupied on the average by half an atom, would give still a little lower potential energy (-60 cal. per mole instead of -58 cal. per mole; see figure 2). In this configuration each atom would have, on the average, six nearest neighbors at a distance of 3.17 \AA .. However there is, of course, no reason that there should be just twice as many places as atoms. I have tried to assume first an undetermined ratio between the number of places and that of atoms, and have then determined the ratio by postulating the minimum of potential energy. It was found to be almost exactly 2. Of course, no particular importance can be attached to such calculations, and I do not want to insist here on one of these particular structures.

The configuration discussed last seems to have some likelihood, as it also agrees quite well with a structure of coordination number 6 recently proposed by Keesom and Takonis (16) on the basis of an x-ray analysis of liquid helium. Keesom describes (cf. figure 2) his structure in terms of a lattice derived from a face-centered lattice, with a density double that of liquid helium, from which half of the atoms have been omitted. He

imagines the λ -point, in the same way as Fröhlich, as an order-disorder transition between the holes and the atoms. However, the same objection raised against Fröhlich's mechanism applies to Keesom's model. The potential energy of the homogeneous statistical distribution of the N atoms over the $2N$ places would also in this case be still lower (-60 cal. per mole) than that of the "ordered" distribution over the sublattice proposed by Keesom (-56 cal. per mole). Moreover, the kinetic zero point energy would again be smaller for the equiform distribution.

Since the atomic distances to the nearest neighbors of Keesom's model are identical with those in the homogeneous statistical distribution, the rather diffuse x-ray exposures speak for our structure equally well.

It might be explicitly stated that the statistical structures that we have met here have, of course, nothing to do with thermodynamic disorder. In principle the whole system is supposed to be representable by a *single* quantum state, which, if it is the lowest state, will describe the system at the absolute zero. Accordingly, there the system has zero entropy in spite of the fact that it may involve a statistical distribution of N atoms over $2N$ places. Quantum-mechanical uncertainty holds, of course, at absolute zero, but it has nothing to do with thermodynamic disorder and entropy.

Since Fröhlich's explanation of the λ -phenomenon fails, the problem remains open as to what particular ordering process could be connected with this anomaly. One might think that this ordering process could be represented by the formation of a lattice, if not of atoms, at least of "places" (possibly of $2N$ places), such as we have described. However, this does not seem likely. If the $2N$ places were to be represented by an exact periodic lattice, i.e. with long-distance order, the x-ray exposures should give interferences with *sharp* lines, like those for the solid state (16), whereas in reality the lines above and below the λ -point have been found to be equally diffuse. There is, so far, no indication of the presence of any ordering process relative to the spatial distribution of the atoms in the liquid at the λ -point.

IV. A MODEL OF LIQUID HELIUM

Resuming the preliminary discussion given in the preceding paragraphs, we may depict liquid helium roughly by the following model. Each helium atom may be imagined as moving in a self-consistent van der Waals field formed by the other atoms, which field contains so much open space and such low potential barriers that the states of the atom in question will be spread over the entire volume of the liquid. Its wave functions will somewhat resemble those of the electrons in metals, or, perhaps, rather those in metallic liquids. They will look approximately like Bloch waves: *viz.*, progressive plane deBroglie waves $e^{2\pi i k x}$, multiplied by a modulated amplitude coming from the swell of the mean field of the other atoms.

The self-consistent field as a whole will, for its part, make quantized elastic Debye vibrations. The distribution of the $3N$ degrees of freedom between the two classes of states may depend on temperature, but we will disregard such details here. The subdivision into the two classes is certainly a quite rough idealization, and there will be, of course, a rather strong interaction between these two types of states.

We may say that this model describes liquid helium by picturing it as a metal in which both the ions and the electrons are replaced by particles of the same kind, namely, helium atoms.

The Debye states will give rise to a contribution to the specific heat, which, at lowest temperatures, is proportional to T^3 . To this we have to add the specific heat of the "electronic" states.

As in the elementary theory of metals, we may first assume, for the lowest of these "electronic" states, an energy spectrum similar to that of free particles,

$$E = \frac{k^2 \hbar^2}{2M} \quad (k = \text{wave number per centimeter}) \quad (3)$$

where M is not necessarily the ordinary mass of the particle, but possibly a certain "reduced" mass. However, unlike the case of electrons in metals, we have to apply here, to the case of helium atoms, Bose-Einstein statistics instead of Fermi statistics.⁴

V. THE BOSE-EINSTEIN CONDENSATION

In his papers on gas degeneracy (1924-1925) Einstein mentioned a peculiar condensation phenomenon of the "ideal" Bose-Einstein gas. This interesting discovery, however, has been almost entirely forgotten in the meantime, probably because Uhlenbeck (26) questioned the correctness of Einstein's argument. Since from the very first the mechanism seemed devoid of any practical significance, all real gases being condensed at the temperature in question, the matter has never been reexamined and it has been generally believed that there is no such condensation phenomenon. If the λ -phenomenon of liquid helium had been discovered between 1925 and 1927, one would perhaps have tried at once to interpret it as the condensation predicted by Einstein. As the matter stands thus far, it has not been recognized that an ideal Bose-Einstein gas actually shows a discontinuity in the derivative of the specific heat (9, 27).

In figure 5 the specific heat, C_v , of an ideal Bose-Einstein gas is represented (19, 20) as a function of T/T_0 , where the "critical temperature" T_0 is defined by:

$$T_0 = \frac{\hbar^2}{2\pi M k} \left(\frac{N}{2.612V} \right)^{2/3} \quad (4)$$

⁴ For the Debye vibrations one need not consider Bose-Einstein statistics explicitly, as there it does not lead to noticeable effects.

With M = the mass of a helium atom, with the molecular volume $V = 27.6$ cc., and N = Avogadro's number, one obtains $T_0 = 3.14^\circ$. The specific heat is given by

$$C_{v-} = 1.92 kN(T/T_0)^{3/2} \quad \text{for } T \leq T_0 \quad (5a)$$

$$C_{v+} = 3/2 kN \{ 1 + 0.231(T_0/T)^{3/2} + 0.045(T_0/T)^3 + 0.040(T_0/T)^{9/2} + \dots \} \quad \text{for } T \geq T_0 \quad (5b)$$

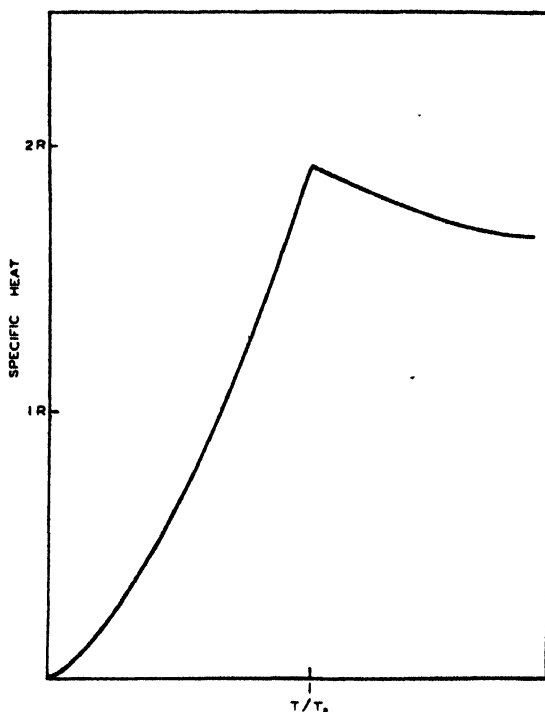


FIG. 5. Specific heat (C_v) of an ideal Bose-Einstein gas

and the entropy

$$S_- = 1.285 kN(T/T_0)^{3/2} \quad \text{for } T \leq T_0 \quad (6a)$$

$$S_+ = \frac{3}{2} kN \{ 1 + \ln(T/T_0) - 0.154(T_0/T)^{3/2} - 0.0150(T_0/T)^3 - 0.0089(T_0/T)^{9/2} - \dots \} \quad \text{for } T \geq T_0 \quad (6b)$$

The entropy at the critical temperature, T_0 , amounts to $1.28 kN$ independent of the value of T_0 .

What is happening to the molecules at the critical temperature, T_0 , can

be indicated most simply by giving their velocity distribution. For $T > T_0$ it is given by the well-known formula:

$$N(v) dv = \frac{2\pi VM^3}{h^3} \frac{v^2 dv}{e^{\gamma v^2 + \alpha} - 1} \quad \left(\gamma = \frac{M}{2kT} \right) \quad (7)$$

where α is to be determined by the condition

$$\int_0^\infty N(v) dv = N$$

At the temperature $T = T_0$, one obtains $\alpha = 0$. For lower temperatures, $T < T_0$, the distribution *splits into two different branches*. A *finite* fraction of all atoms, namely,

$$N_0 = N [1 - (T/T_0)^{\frac{1}{2}}] \quad (8a)$$

have the velocity $v = 0$, whereas the remainder are distributed in a way similar to the ordinary distribution, *viz.*:

$$N(v) dv = \frac{2\pi VM^3}{h^3} \frac{v^2 dv}{e^{\gamma v^2} - 1} \quad (v > 0) \quad (8b)$$

If one likes analogies, one may say that for $T < T_0$ there is actually a kind of condensation, not in ordinary space but in the space of velocities, i.e., an equilibrium of two phases: *one* containing the molecules N_0 representing, so to speak, a state of higher order,—all molecules having the same velocity, zero; and *another one* showing a distribution over all velocities similar to that which is realized for $T > T_0$. In ordinary space, however, no separation of phases, no change of order, is to be noticed.

VI. POSSIBLE SIGNIFICANCE FOR THE λ -PHENOMENON OF LIQUID HELIUM

Although actually the λ -point of helium shows a much sharper discontinuity and rather resembles a *jump* more than a break in the course of the specific heat, it seems difficult not to imagine a connection with the condensation phenomenon of the Bose-Einstein statistics. The theoretical values of 3.14° A. and $1.28 R$ for the critical temperature of the *ideal* Bose-Einstein gas and for the entropy at this temperature differ from the experimental data of the λ -point (2.19° A. and $0.8 R$) in such a way as to inspire trust. It may be mentioned that any alteration concerning the supposed density of the lowest energy levels would have a very great influence upon the shape of the discontinuity. Thus, if the density of states, in the limit for very small wave number k , is supposed to be proportional to $k^4 dk$ (instead of proportional to $k^2 dk$ as for free particles), the Bose-Einstein statistics yields not a break, but a real *jump* in the specific heat curve. Such a decrease in the density of the levels for the lowest

states is quite probable, since the introduction of any interaction between the atoms would produce such an effect. In particular it seems that the "exchange forces," which are coördinate with the van der Waals forces (thus far never investigated), would account for the fact that in reality the ordering process proceeds still more rapidly than would follow from the theory of degeneration of an "ideal" Bose-Einstein gas. These exchange forces have the character of an *attraction in space of velocities* (i.e., their interaction energy is always negative and disappears with large relative velocity), provided the particles obey Bose statistics, and such an interaction would indeed favor the ordering process we have just described.

Let us anticipate the presumable result of the introduction of such an interaction, and assume the density of the lowest states of the Bloch type to be given by the number of states in the energy interval $(\epsilon, \epsilon + d\epsilon)$:

$$g(\epsilon) d\epsilon = AV \epsilon^{\sigma-1} d\epsilon \quad (9)$$

Here A and σ are adjustable constants ($\sigma > 2$). From this assumption we obtain for the specific heat:

$$C_{v-} = kN'\sigma(\sigma + 1) \frac{\zeta_{\sigma+1}}{\zeta_{\sigma}} (T/T_0)^{\sigma} \quad \text{for } T < T_0 \quad (10a)$$

$$C_{v+} = kN'\sigma \left\{ 1 + \frac{\sigma - 1}{2^{\sigma+1}} \zeta_{\sigma}(T_0/T)^{\sigma} + (2\sigma - 1) \left(\frac{2}{3^{\sigma+1}} - \frac{1}{2^{2\sigma}} \right) \zeta_{\sigma}^2(T_0/T)^{2\sigma} + \dots \right\} \quad \text{for } T > T_0 \quad (10b)$$

In particular for $T = T_0$ the convergence of the above series is very bad. There the value of C_{v+} is given by

$$C_{v+}(T_0) = kN'\sigma \left\{ (\sigma + 1) \frac{\zeta_{\sigma+1}}{\zeta_{\sigma}} - \sigma \frac{\zeta_{\sigma}}{\zeta_{\sigma-1}} \right\} \quad (10b')$$

Here ζ_0 is defined by the series $\zeta_{\sigma} = 1 + \frac{1}{2^{\sigma}} + \frac{1}{3^{\sigma}} + \frac{1}{4^{\sigma}} + \dots$ and T_0 by

$$T_0 = \frac{1}{k} \left[\frac{N'}{\zeta_{\sigma} AV (\sigma - 1)!} \right]^{1/\sigma} \quad (11)$$

N' will no longer be Avogadro's number, but rather the number of particles in Bloch states per molecular volume V .

$$N_0 = N' [1 - (T/T_0)^{\sigma}] \quad (12)$$

is, for $T \leq T_0$, the number of particles that are condensed in the lowest state.

The discontinuity of the specific heat is given by

$$\left(\frac{C_{v-}}{C_{v+}}\right)_{T=T_0} = \frac{1}{1 - \frac{\sigma}{\sigma+1} \frac{\xi_\sigma^2}{\xi_{\sigma-1}\xi_{\sigma+1}}} \quad (13)$$

The experimental values for the specific heat of liquid helium suggest a value of $\sigma \sim 5$ and of $N' = 0.136 N$ (figure 6).

One need not think that the basis of the theory has been abandoned by such a modification of the energy spectrum. The Bose statistics is

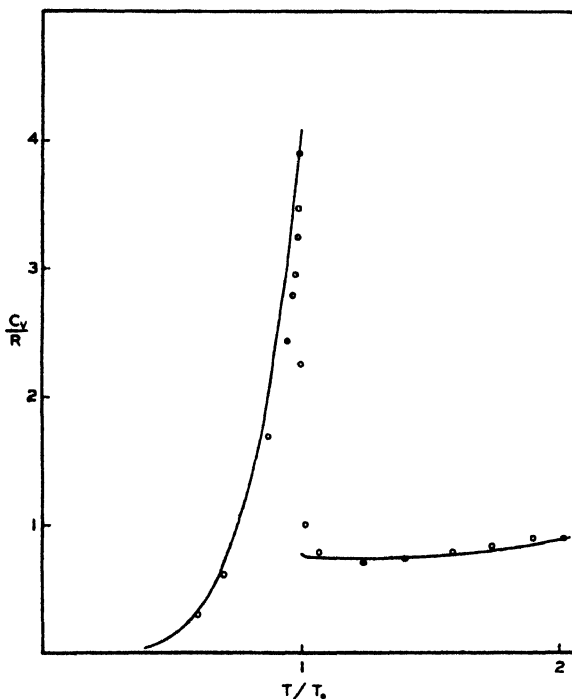


FIG. 6. Specific heat (C_v) for Bose-Einstein statistics. $\sigma = 5$; $N' = 0.136N$ plus a Debye term $0.0231RT^3$. The circles give the experimental values for helium (13).

and remains throughout essential for the occurrence of the discontinuity. In Boltzmann or in Fermi statistics the introduction of a modified spectrum such as (9) would not give rise to a similar phenomenon.

VII. SUPERFLUIDITY

A real decision for or against our hypothesis will only be possible when its consequences for the strange transport phenomena of liquid helium have been worked out. Thus far only a quite elementary discussion has been attempted. This preliminary discussion, however, entitles one to

believe that the peculiarities of a degenerate Bose-Einstein gas might, in any case, be strange enough to be capable of reproducing even such strange phenomena as have actually been found with liquid helium.

Let us go back to our model of section IV, representing liquid helium as a metal, in which the ions as well as the electrons are both replaced by helium atoms. We need not discuss in detail here to what extent this model gives a simplified picture of the real state of affairs. We may trust that, as often happens in physics, the consequences and connections derived for our extremely simplified model will prove to be in a high degree independent of the special assumptions we found ourselves forced to introduce.

The fluidity of our model liquid will correspond to the electrical conductance of the electrons in a metal: The friction will be due to the dissipation of progressive Bloch waves by inelastic collisions with the Debye waves. Let us make the assumption that for these collisions a mean free path l might exist, which is independent of the velocity v for small values of v .

The well-known formula for the conductivity $\sigma \sim \overline{l/v}$ would yield the value $\sigma \rightarrow \infty$ in the case where a finite fraction of all particles has velocity zero. But actually one has to apply a special consideration for the slowest particles. A particle of mass M and of initial velocity v_0 , chosen in the direction of the field F , needs the time τ to traverse the mean free path l :

$$l = v_0\tau + \frac{1}{2M} F\tau^2$$

or

$$\tau = \frac{M}{F} [\sqrt{v_0^2 + 2lF/M} - v_0]$$

The mean change of velocity due to the action of F during this time τ will therefore be given by

$$\overline{\delta v_0} = \frac{1}{M} F \cdot \tau/2 = \frac{1}{2} [\sqrt{v_0^2 + 2lF/M} - v_0] \quad (14)$$

In general (particularly in the case of Fermi statistics, and also in the case $T > T_0$ for the Bose statistics), one is accustomed and entitled to disregard the few particles with $\frac{M}{2} v_0^2 \leq l \cdot F$ and one may write:

$$\overline{\delta v_0} = \frac{l}{2Mv_0} \cdot F \quad \text{for } \frac{M}{2} v_0^2 \gg l \cdot F \quad (14a)$$

which gives the above mentioned formula for σ .

In the case of the Bose degeneracy ($T < T_0$), however, a *finite fraction* of all particles has the velocity $v_0 = 0$. For these we obtain

$$\overline{\delta v_0} = \sqrt{\frac{lF}{2M}} \quad \text{for } \frac{M}{2} v_0^2 \ll lF \quad (14b)$$

This contribution is, for a fixed small value of F , enormously greater than equation 14a. One may say that the conductivity, *viz.*, the fluidity (defined as derivative of the current with respect to F) becomes infinite in the limit $F \rightarrow 0$.

For a fixed value of F the dependence of the fluidity on temperature should be proportional to the number N_0 of particles in the lowest state. If the specific heat is given by equation 10a

$$C_- \sim (T/T_0)^\sigma$$

the number N_0 is proportional to

$$N_0 = \begin{cases} N [1 - (T/T_0)^\sigma] & \text{for } T < T_0 \\ \sim 0 & \text{for } T > T_0 \end{cases}$$

and accordingly the superfluid current should be proportional to $1 - (T/T_0)^\sigma$, for $T < T_0$, and disappear for $T > T_0$ (figure 7).

VIII. THERMOMECHANICAL EFFECT

The particles N_0 , having the energy zero, will not appreciably contribute to the transport of energy, and therefore one should not expect a particularly great increase of the heat conductivity when passing to the degenerate state.

But there is another mechanism which may produce a transfer of heat (21). The van der Waals forces between the walls and the helium atoms are much stronger than those between the helium atoms themselves. Therefore in a layer, L , of 10 Å. or 100 Å. or perhaps even greater thickness along the walls, the van der Waals field will be appreciably stronger than in the interior, I , of the liquid. In this layer the concentration of the degenerate atoms will therefore be much greater than in the interior, and accordingly the entropy in the layer, S_L , will be much smaller than in the interior, S_I . Thus we have a situation quite analogous to a thermocouple,—namely, two different conductors, L and I , in conducting contact.

If q moles of helium pass at a temperature T from I to L , they will go into a state of greater order and the heat

$$Q = T (S_I - S_L)q \quad (15)$$

will be set free. This will occur in a *reversible manner*, quite as in the case of the Peltier effect. Relating all transfer of energy or matter to unit

of time and to unit of cross section, we may write

$$Q = T(S_I - S_L)J \quad (15')$$

where J is the current density. The Peltier coefficient is accordingly given by

$$\Pi_{I,L} = T(S_I - S_L) \quad (16)$$

Assuming for the specific heat the expression 10a we obtain for the entropy:

$$S_- = \text{Const. } T^\sigma V \quad (17)$$

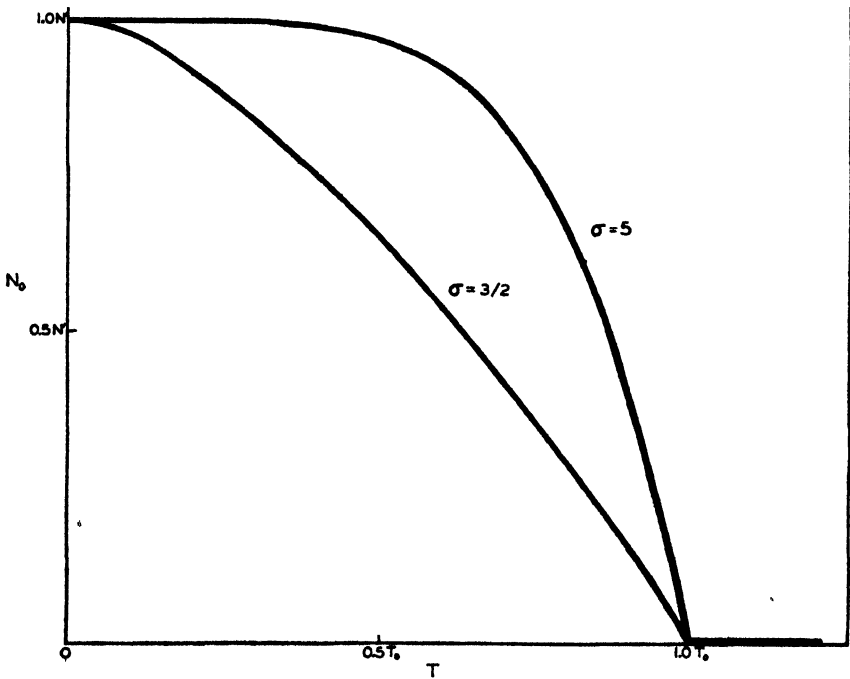


FIG. 7. Population of the lowest state ($\sigma = 3/2$ and $\sigma = 5$)

and accordingly for the Peltier coefficient

$$\Pi_{I,L} = \text{Const. } T^{\sigma+1}(V_I - V_L) \quad (18)$$

Now the arrangement for measuring heat conductivity can simply be considered as a thermocouple consisting of the two "metals" L and I . If we heat the wall at *one* point and cool at another one, in such a way that the temperature at the two points may be kept constant at T_1 and T_2 , respectively, we may produce a "thermo-force", Φ , given, according to

W. Thomson's well-known thermodynamic relation, by the formula

$$\Phi = \int_1^{T_2} \frac{\Pi_{I,L}}{T} dT = \int_{T_1}^{T_2} (S_I - S_L) dT$$

or, with equation 17,

$$= \text{Const} \cdot T^\sigma (T_2 - T_1)(V_I - V_L)$$

This "thermo-force" will produce a considerable circulation of matter, since the "internal resistance" of the thermoelement is extraordinarily small, and therefore the consumption of heat for maintaining even the smallest temperature differences will also be considerable. This process, therefore, will appear like an enormous heat conduction which, however, will depend very strongly on the gradient of temperature. Actually one has found such variations of heat conductivity with the temperature gradient (3, 15). For the lowest temperatures the helium atoms will everywhere be almost completely degenerate, in the layer as well as in the interior of the liquid. There will be no difference of entropy between the different parts of the liquid; the "Peltier heat" as well as the "thermo-force" will disappear—as it must according to Nernst's law—and there will no longer be a production of circulation in the liquid. Only ordinary heat conductivity (chiefly by Debye vibrations) will remain. Nevertheless the great fluidity will persist down to the lowest temperatures, since it is proportional to $N_0 \sim 1 - (T/T_0)^\sigma$; only the thermo-force disappears (proportional to T^σ).

All this is in complete qualitative agreement with the experiments, particularly with those of Keesom (15) and of Kürti and Simon (17), on the heat conductivity of helium at the lowest temperatures, which, below 0.6°A. , has been found to become "normal" again, i.e., independent of the gradient of temperature. In fact this transition to normal heat conductivity occurs in just that region where the thermal anomaly of the specific heat, connected with the λ -point, ceases and passes over into an ordinary Debye T^3 -law for the specific heat. In figure 8 we have plotted the product of the Peltier coefficient TS times the number of degenerate atoms, N_0 , against temperature. This product, in any case, will form a factor characteristic of the transported heat, regardless of the result of a future vigorous treatment of the mean free path problem.

This mechanism of reversible transformation of heat into mechanical energy gives a very simple explanation also of the so-called "fountain phenomenon" observed by Allen and Jones (1), and interprets it as a pump driven by a thermoelement. It may be remarked that the flow of matter in the capillary layer has to have the opposite direction to the transfer of heat, if the entropy in the capillary layer is smaller than in the

normal liquid. In fact this connection between the flow of heat and the flow of matter is actually realized in the experiment of Allen and Jones.

It may be mentioned that the idea that the transport phenomena of helium II might be reversible processes was first discussed by Tisza (25). The thermodynamic relation (equation 15) has recently been given by H. London (21). Though it might appear that the logical connection between the facts will not be qualitatively very different from the one we have sketched here, it is obvious that the theoretical basis given thus far

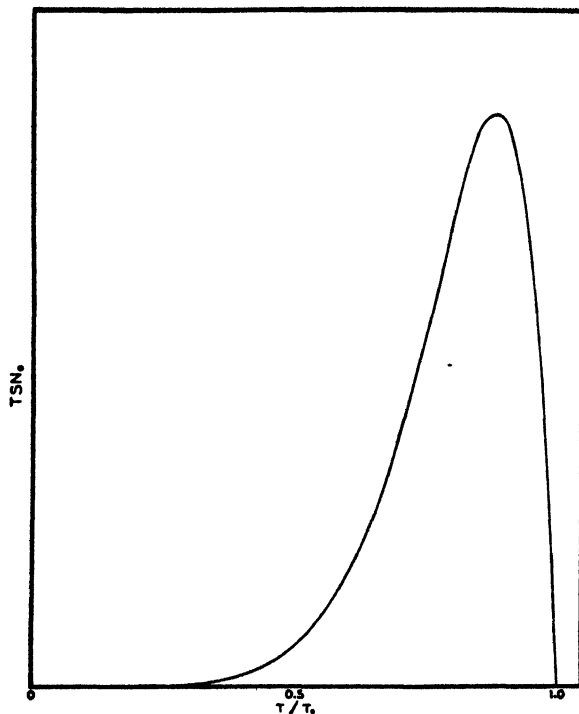


FIG. 8. TSN_0 as a function of T ($\sigma = 5$)

is not to be considered more than a quite rough and preliminary approach to the problem of liquid helium, limited chiefly by the lack of a satisfactory molecular theory of liquids.

IX. SUMMARY

It has recently been shown that, contrary to current views, an ideal Bose-Einstein gas shows a discontinuity in the course of its specific heat curve. This anomaly is connected with a kind of condensation process first mentioned by Einstein. Some evidence has been given to support the idea that the peculiar phase transition (λ -point) liquid helium undergoes

at 2.19° K. might be regarded as the condensation phenomenon of the Bose-Einstein statistics, distorted, of course, owing to the fact that it manifests itself in the liquid and not in the gaseous state.

Further evidence in favor of this interpretation is furnished by an elementary discussion of the transport properties of the condensed phase. It is shown that the theory might account for the sudden increase of the fluidity and of the heat conductivity when going below the λ -point. The latter phenomenon comes out, not as an ordinary heat conductivity, but rather as a reversible phenomenon, similar to the heat transport in a thermoelement, namely, as a reversible transformation of heat into mechanical work. This thermomechanical effect also furnishes the explanation of the so-called "fountain phenomenon" discovered by Allen and Jones.

REFERENCES

- (1) ALLEN, J. F., AND JONES, H.: *Nature* **141**, 243 (1938).
- (2) ALLEN, J. F., AND MISENER, A. D.: *Nature* **141**, 75 (1938).
- (3) ALLEN, J. F., PEIERLS, R., AND UDDIN, M. Z.: *Nature* **140**, 62 (1937).
- (4) BURTON, E. F.: *Nature* **135**, 265 (1935).
- (5) BURTON, E. F.: *Nature* **142**, 72 (1938).
- (6) DAUNT, J. G., AND MENDELSSOHN, K.: *Nature* **141**, 911 (1938); **142**, 475 (1938).
- (7) EINSTEIN, A.: *Ber. Berl. Akad.* **1924**, 261; **1925**, 3.
- (8) FRÖHLICH, H.: *Physica* **4**, 639 (1937).
- (9) KAHN, B.: Thesis, University of Utrecht, 1938.
- (10) KAPITZA, P.: *Nature* **141**, 74 (1938).
- (11) KEESOM, W. H., AND CLUSIUS, K.: *Commun. Kamerlingh Onnes Lab. Univ. Leiden* **219** (1932).
- (12) KEESOM, W. H., AND KEESOM, H. P.: *Proc. Acad. Sci. Amsterdam* **35**, 736 (1932).
- (13) KEESOM, W. H., AND KEESOM, H. P.: *Physica* **2**, 557 (1935).
- (14) KEESOM, W. H., AND KEESOM, H. P.: *Physica* **3**, 359 (1936).
- (15) KEESOM, W. H., KEESOM, A. D., AND SARIS, B. F.: *Physica* **5**, 281 (1938).
- (16) KEESOM, W. H., AND TAKONIS, K. W.: *Physica* **5**, 161, 270 (1938).
- (17) KÜRTI, N., AND SIMON, F.: *Nature* **141**, 207 (1938).
- (18) LONDON, F.: *Proc. Roy. Soc. (London)* **A153**, 576 (1936).
- (19) LONDON, F.: *Nature* **141**, 643 (1938).
- (20) LONDON, F.: *Phys. Rev.* **54** (December, 1938).
- (21) LONDON, H.: *Nature* **142**, 612 (1938).
- (22) ROLLIN, B. V.: *Physica* **3**, 296 (1936).
- (23) SIMON, F.: *Nature* **133**, 460, 529 (1934).
- (24) SLATER, T. C., AND KIRKWOOD, J. G.: *Phys. Rev.* **37**, 682, 832 (1931).
- (25) TISZA, L.: *Nature* **141**, 913 (1938).
- (26) UHLENBECK, G. E.: Dissertation, University of Leiden, 1927.
- (27) UHLENBECK, G. E., AND KAHN, B.: *Physica* **5**, 399 (1938).
- (28) WILHELM, J. O., MISENER, A. D., AND CLARK, A. R.: *Proc. Roy. Soc. (London)* **A151**, 342 (1935).

STATISTICAL MECHANICS OF CONDENSING SYSTEMS. V¹

TWO-COMPONENT SYSTEMS

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I. INTRODUCTION

An extension of the method of Ursell (8) for treating imperfect gases has been developed by the author, working with Ackermann and with Harrison (5, 6, 7). This method has succeeded in predicting the conditions under which condensation occurs in a one-component system, and is in agreement with experiments showing that the usual classical conception of the critical point is not altogether correct (3). The theory was reported by Born (1) to the van der Waals Congress in Amsterdam. Since then Born has, with Fuchs (2), greatly improved its mathematical basis, as have also Kahn and Uhlenbeck (4). In this paper the method, with a mathematical approach modelled after that of Born and Fuchs, will be applied to two-component systems.

In general, for any system, the work function A , or Helmholtz free energy, may be calculated as

$$A = kT \left[\ln \prod_i \left(\frac{h^2}{2\pi m_i kT} \right)^{3N_i/2} - \frac{Q_r(N_i, V, T)}{\prod_i N_i!} \right] \quad (1)$$

in which N_i is the number of molecules of type i . Q_r , the volume-dependent part of the expression, is the configuration integral of the system, an integral over the configuration space of the molecules.

For the usual classical mechanical case Q_r is given as

$$Q_r = \int \int \cdots \int e^{-U/kT} d\tau_1 \cdots d\tau_i \cdots d\tau_N \quad (2)$$

in which U is the potential energy of the system as a function of the coordinates of the molecules, and $d\tau_i$ is the element of configuration space of

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the j^{th} molecule in the system composed of N molecules. For the simple case of monatomic molecules with no internal degrees of freedom

$$d\tau_j = dx_j dy_j dz_j \quad (3)$$

For the sake of simplicity of expression we shall limit ourselves to cases for which equation 3 is valid.

The essential feature of the method followed is to split the integrand, $e^{-U/kT}$, of equation 2 into a sum of terms, the first being unity throughout the configuration space, the others differing from zero only where certain numbers, m_l , of clusters of l specified molecules each are close to each other in the cluster. In the case that the potential U of the system is a sum of $\frac{1}{2}N(N-1)$ terms, each a function only of the one distance between one pair of molecules, this analysis into a sum of terms can be made readily from the mathematical form of the integrand. The integral of such a general term in this sum is a product of "cluster integrals," Nvb_l , each raised to the power m_l , where v is the volume per molecule in the system. Kahn and Uhlenbeck have shown this to be a general result, independent of the use of the classical expression (equation 2) for Q_r , and independent of the assumption that the potential is the sum of that between molecule pairs.

Those terms characterized by the same set of numbers m_l , but with different specified molecules associated together in the clusters, lead to the same integral in a one-component system, and correspond all to one definite distribution of the molecules in the configuration space. This distribution is simply one in which there are m_l clusters, each containing l molecules close to each other, in excess of the random expectation. Distributions described in this way are naturally significant only as long as the total volume is so large that some of the molecules, at least, are at distances large compared to the reach of the molecular forces from any neighbor. It is therefore not surprising that the method fails to give simple results, at least without forcing, for volumes lower than that of the condensed phase.

If there are two types of molecules, with a total of L molecules of type a , and Λ molecules of type α , in the system, with

$$L + \Lambda = N \quad (4)$$

we must distinguish the clusters by two numbers, l and λ , the numbers of molecules of types a and α , respectively, in the cluster.

The number of numerically equal terms in the integral Q_r , with the same set of the numbers $m_{l,\lambda}$ of clusters of l and λ molecules each of types a and α , respectively, is just the number of ways in which the L and Λ numbered

molecules of the two types can be distributed among the clusters. This leads to a numerical coefficient for each product

$$\prod_{l,\lambda} (Nvb_{l,\lambda})^{m_{l,\lambda}}$$

in Q_r , such that

$$\frac{Q_r(L, \Lambda, vb)}{L! \Lambda!} = \sum_{\substack{m_{l,\lambda} \\ \sum l m_{l,\lambda} = L \\ \sum \lambda m_{l,\lambda} = \Lambda}} \prod_{l,\lambda} \frac{(Nvb_{l,\lambda})^{m_{l,\lambda}}}{m_{l,\lambda}!} \quad (5)$$

The cluster integrals, $b_{l,\lambda}$, are volume-independent at large volumes. The volume per molecule v_f , below which the $b_{l,\lambda}$'s become significantly volume-dependent, is that of the condensed phase. We shall assume, in the subsequent discussion, that v is always greater than v_f .

It is only in the case that the potential U may be written as a sum of interactions u_{aa} , $u_{a\alpha}$, and $u_{\alpha\alpha}$ between pairs of types aa , $a\alpha$ and $\alpha\alpha$,

$$U = \sum_{n>m} \sum_{m=1}^{L-1} u_{aa}(r_{mn}) + \sum_{\mu=1}^{\Lambda} \sum_{m=1}^L u_{a\alpha}(r_{m\mu}) + \sum_{\nu>\mu}^{\Lambda} \sum_{\mu=1}^{\Lambda-1} u_{\alpha\alpha}(r_{\mu\nu}) \quad (6)$$

that the integral definition of the $b_{l,\lambda}$ can be readily given. Defining

$$f_{aa}(r_{mn}) = f_{mn} = e^{-u_{aa}(r_{mn})/kT} - 1 \quad (7a)$$

$$f_{a\alpha}(r_{m\mu}) = f_{m\mu} = e^{-u_{a\alpha}(r_{m\mu})/kT} - 1 \quad (7b)$$

$$f_{\alpha\alpha}(r_{\mu\nu}) = f_{\mu\nu} = e^{-u_{\alpha\alpha}(r_{\mu\nu})/kT} - 1 \quad (7c)$$

the equation for $b_{l,\lambda}$ is

$$b_{l,\lambda} = \frac{1}{Vl!\lambda!} \int \cdots \int \sum \Pi f_{mn} f_{m\mu} f_{\mu\nu} dt_1 \cdots dt_l d\tau_1 \cdots d\tau_\lambda \quad (8)$$

(sum over all products consistent with a single cluster)

in which dt is used for the element of configuration space of molecules of type a , and $d\tau$ for molecules of type α . The sum goes over all possible products of the f 's, such that all molecules are at least singly connected with functions f to every other. The integrals $b_{l,0}$ and $b_{0,l}$ are identical in form with that written as b_l in previous papers on one-component systems.

For the classical case, equation 2, and when expression 6 is assumed for U , irreducible integrals $B_{k,\kappa}$ may be defined as

$$B_{k,\kappa} = \frac{1}{Vk!\kappa!} \int \int \cdots \int \sum \Pi f_{mn} f_{m\mu} f_{\mu\nu} dt_1 \cdots dt_k d\tau_1 \cdots d\tau_\kappa \quad (9)$$

(sum over all products with all molecules more than singly connected)

The cluster integrals $b_{l,\lambda}$ can be shown to be sums of products of the $B_{k,\kappa}$ raised to certain powers. These integrals, $B_{k,\kappa}$, differ from the irreducible integrals β_k of the earlier papers for one-component systems in their normalization. The two notations are so related that $B_{k,0}$ and $B_{0,k}$ are the same as $\beta_{(k-1)}/k$.

The numerical coefficient with which a certain product of irreducible integrals $B_{k,\kappa}$ occurs in the cluster integral $b_{l,\lambda}$ is not easy to evaluate or simple to express in closed analytical form when evaluated. In appendix B these coefficients are calculated, and $b_{l,\lambda}$ is derived in terms of the $B_{k,\kappa}$ as a Cauchy integral. This form (equation B-23) is sufficiently explicit for our purposes.

Of course it would be formally possible to define the quantities $B_{k,\kappa}$ in terms of the integrals $b_{l,\lambda}$ by the inverse of equation B-23. By this artifice the irreducible integrals are definable even when equation 6 is not valid or even in the quantum-mechanical case that Q_r is not given by equation 2. The subsequent equations of this article are therefore formally valid under all conditions, but, as pointed out by Kahn and Uhlenbeck, this seems extremely artificial.

Certain sums, related to the g_r sums of previous articles, occur repeatedly in the equations. These sums occur both as functions of the $b_{l,\lambda}$ with certain variables z and ζ , and also as functions of $B_{k,\kappa}$ with other variables y and η . In order to shorten the notation the two cases will be distinguished by using lower case and capital letters, respectively. The sums are defined as

$$g_{m,\mu} = \sum_{l=0}^{\infty} \sum_{\lambda=0}^{\infty} l^m \lambda^{\mu} b_{l,\lambda} z^l \zeta^{\lambda} \quad (b_{0,0} = 0) \quad (10a)$$

$$G_{m,\mu} = \sum_{k=0}^{\infty} \sum_{\kappa=0}^{\infty} k^m \kappa^{\mu} B_{k,\kappa} y^k \eta^{\kappa} \quad (B_{k,\kappa} = 0 \text{ if } k + \kappa < 2) \quad (10b)$$

The relationships

$$g_{m,\mu} = z \left(\frac{\partial}{\partial z} \right)_{\zeta} g_{(m-1),\mu} = \zeta \left(\frac{\partial}{\partial \zeta} \right)_z g_{m,(\mu-1)} \quad (11a)$$

$$G_{m,\mu} = y \left(\frac{\partial}{\partial y} \right)_{\eta} G_{(m-1),\mu} = \eta \left(\frac{\partial}{\partial \eta} \right)_y G_{m,(\mu-1)} \quad (11b)$$

are seen to hold from the definitions 10a and 10b of the sums.

II. THE METHOD OF USING THE LOGARITHM OF THE LARGEST TERM IN Q_r

Expression 5 for Q_r consists of a sum of terms, each characterized by a certain set of the numbers $m_{l,\lambda}$ defining a distribution of the molecules in space.

The logarithm of Q_r , for large values of L and Λ , may be equated to that

of the largest term in the sum. The largest term, subject to the conditions that $\Sigma \lambda m_{i,\lambda} = L$ and $\Sigma \lambda m_{i,\lambda} = \Lambda$, is found by the method of undetermined multipliers, using the symbols $\ln z$ and $\ln \zeta$ for the two parameters. The details of the manipulation do not differ appreciably from those used previously for one-component systems (5), and will not be repeated.

One obtains for the quantity $a(x)$, defined as

$$\begin{array}{l} \text{limit at constant} \\ x = L/N, x = \Lambda/N \left[-\frac{1}{N} \ln \frac{Q_r(L, \Lambda, vb)}{L! \Lambda!} \right] = a(x) \\ \text{as } N \rightarrow \infty \end{array} \quad (12)$$

the equation

$$a(x) = x \ln z + \chi \ln \zeta - v g_{0,0} \quad (13)$$

($x + \chi = 1$), in which z and ζ are determined by the two equations,

$$g_{1,0} = \frac{x}{v} \quad (14a)$$

$$g_{0,1} = \frac{\chi}{v} \quad (14b)$$

From equation 1 the quantity $a(x)$ is seen to be related to the work function A , per mole of material, by the equation

$$a(x) = \frac{A}{RT} - x \ln \left(\frac{h^2}{2\pi m_a kT} \right)^{3/2} - \chi \ln \left(\frac{h^2}{2\pi m_a kT} \right)^{3/2} \quad (15)$$

so that

$$A = RT \left[x \ln \left(\frac{h^2}{2\pi m_a kT} \right)^{3/2} z + \chi \ln \left(\frac{h^2}{2\pi m_a kT} \right)^{3/2} \zeta - v g_{0,0} \right] \quad (16)$$

The pressure,

$$\begin{aligned} P = - \left(\frac{\partial A}{\partial V} \right)_T &= - kT \left(\frac{\partial a(x)}{\partial v} \right)_T = \\ &= kT \left[g_{0,0} + (x - v g_{1,0}) \frac{\partial \ln z}{\partial v} + (\chi - v g_{0,1}) \frac{\partial \ln \zeta}{\partial v} \right] \end{aligned}$$

is found to be, with the use of equations 14a and 14b,

$$P = kT g_{0,0} \quad (17)$$

The equation for the free energy, F , per mole is

$$F = A + PV = RT \left[x \ln \left(\frac{h^2}{2\pi m_a kT} \right)^{3/2} z + \chi \ln \left(\frac{h^2}{2\pi m_a kT} \right)^{3/2} \zeta \right] \quad (18)$$

so that the chemical potentials μ_a and μ_α of the two molecular species are

$$\mu_a = kT \ln \left(\frac{h^2}{2\pi m_a kT} \right)^{3/2} z \quad (19a)$$

$$\mu_\alpha = kT \ln \left(\frac{h^2}{2\pi m_\alpha kT} \right)^{3/2} \zeta \quad (19b)$$

which shows the physical significance of z and ζ .

The two sums $g_{1,0}$ and $g_{0,1}$ (equations 14a and 14b) will be convergent for sufficiently large values of v . Under these conditions the system will be one phase gaseous. The condensation volume v_s , the volume per molecule of the saturated vapor, will be determined by that value of v for which $g_{1,0} + g_{0,1}$ becomes divergent.

For $v > v_s$ the quantities z and ζ may be expressed as power series in $1/v$, and the first few coefficients determined from equations 14a and 14b by algebraic methods. If these coefficients are expressed in the $B_{k,\lambda}$'s instead of the $b_{l,\lambda}$'s (which can be done without great difficulty, since the expressions for the lower $b_{l,\lambda}$'s in terms of the $B_{k,\lambda}$'s are not difficult to evaluate), one finds that the lower terms agree with those of the equations

$$z = ye^{-G_{1,0}/v} \quad (20a)$$

$$\zeta = \eta e^{-G_{0,1}/v} \quad (20b)$$

in which

$$y = \frac{x}{v} \quad (21a)$$

$$\eta = \frac{\chi}{v} \quad (21b)$$

Inserting these values of z and ζ in $g_{0,0}$, and expressing this function as an inverse power series of v , one obtains, with equation 17,

$$P = kT(y + \eta - G_{1,0} - G_{0,1} + G_{0,0}) \quad (22)$$

which is the virial expression for the pressure as an inverse power series in the volume.

This method of using the logarithm of the largest term in Q , for $\ln Q$, has certain advantages. It expresses the thermodynamic properties of the system in terms of the configuration integral over the equilibrium distribution of the molecules in space, and determines this equilibrium distribution. The numbers $m_{l,\lambda}$ of clusters of l and λ molecules of a and α , respectively, in the equilibrium distribution are given by

$$m_{l,\lambda} = N v b_{l,\lambda} z^l \zeta^\lambda \quad (23)$$

so that the individual terms $lvb_{l,\lambda}z^l\zeta^\lambda$ and $\lambda vb_{l,\lambda}z^l\zeta^\lambda$ of $\dot{v}g_{1,0}$ and $v\dot{g}_{0,1}$ are the numbers of molecules of types a and α , respectively, in clusters of types l and λ divided by the total number of molecules in the system.

The method, however, is scarcely convincing mathematically. In the first place, the author is not quite certain that the total number of terms in equation 5 is sufficiently small to permit proof that the method is justifiable even if all the terms are positive, as can be done for a one-component system. Secondly, the method is certainly unjustifiable if some of the $b_{l,\lambda}$'s are negative, which will be the case at sufficiently high temperatures. Thirdly, equations 20 to 22 have not been generally proved, but it has only been shown that as many terms in the power series development of them are correct as have been specifically calculated. Since the difficulty of calculation increases rapidly with the order of the terms, this method is not practical for terms even as low as the order v^{-4} . Fourthly, the values of v , z , and ζ for which $g_{1,0} + g_{0,1}$ diverges, and for which the gas starts to condense, are not readily calculable from the equations.

We shall therefore resort in the next section to a more abstract mathematical method, based on that of Born and Fuchs (2), by which the equations of this section are rigorously proved, and which shows the conditions for condensation.

III. THE EXACT MATHEMATICAL TREATMENT

A rigorous proof of the equations for the system may be developed with the use of four purely mathematical theorems which are proved in appendices A, B, C, and D. These theorems are as follows:

Theorem A: The function defined as

$$H(vb, r, \rho) = \sum_{L=0}^{\infty} \sum_{\Lambda=0}^{\infty} \frac{Q_r(L, \Lambda, vb)}{L! \Lambda!} r^L \rho^\Lambda \quad (24)$$

is equal to

$$H(vb, r, \rho) = \frac{1}{1 - v(g_{1,0} + g_{0,1})} \quad (25)$$

where the quantities z and ζ are now defined by

$$r = ze^{-vg_{0,0}} \quad (26a)$$

$$\rho = \zeta e^{-vg_{0,0}} \quad (26b)$$

Theorem B: The solution to the combinatory problem of finding the coefficients of the powers of irreducible integrals $B_{k,\kappa}$ in $b_{l,\lambda}$ is such that $b_{l,\lambda}$ is given by equation B-23.

Theorem C: From equation B-23 the sums $g_{m,\mu}(b_{l,\lambda}, z, \zeta)$ may be expressed in terms of the sums $G_{m,\mu}$ of the parameters $B_{k,\kappa}$ and variables y and η

defined as functions of z and ζ by equations 20a and 20b, with the equations C-10, C-12, C-13a, and C-13b. The sums $g_{m,\mu}$ and $G_{m,\mu}$ are defined by the equations 10a and 10b. The functions defined as

$$W = y - G_{2,0} + G_{1,0} \quad (27a)$$

$$\Omega = \eta - G_{0,2} + G_{0,1} \quad (27b)$$

$$w = G_{1,1} \quad (28)$$

occur in these equations.

Theorem D: The line of nearest singularity of $H(vb, r, \rho)$ which determines associated radii of convergence r_0 and ρ_0 of the sum (equation 24) is known, from the positivity of the coefficients Q_r , to occur on the real positive axes of all the complex variable pairs,— r, ρ ; z, ζ ; and y, η . The function H is regular for all real positive values of the variables smaller than those satisfying any of the conditions:

$$(a) \quad g_{1,0} + g_{0,1} = \frac{1}{v}$$

$$(b) \quad g_{0,1} + g_{1,0} \text{ singular}$$

which are equivalent to

$$(\alpha) \quad y + \eta = \frac{1}{v}$$

$$(\beta) \quad W\Omega - w^2 = 0$$

$$(\gamma) \quad \text{Any } G_{m,\mu} \text{ singular}$$

The function H is singular if any of these conditions is obeyed.

There remains one point of a mathematical nature to be discussed. In a singly infinite series of one variable the radius of convergence determines the upper limit of the n^{th} root of the coefficients. In the double sum (equation 24) we are interested in the n^{th} root of the coefficient for constant values of the ratio $x = L/N$, the mole fraction of the component a in the system. More specifically we seek the value of the function $a(x)$ defined by equation 12.

The sum (equation 24) goes over all values of the mole fraction x , and diverges at certain associated values r_0 and ρ_0 of its variables r and ρ . Each pair of values r_0, ρ_0 determines $a(x)$ at some x value, but it remains for us to determine which value of x corresponds to a given pair r_0, ρ_0 .

The fact that

$$\frac{\partial^2 a(x)}{\partial x^2} \geq 0 \quad (29)$$

must be used in the argument. Equation 29 follows from the relation (equation 15) between $a(x)$ and the work function A of the system, since it can be seen physically that if equation 29 were not obeyed and the second derivative were negative, the system could separate into two phases of mole fractions x_1 and x_2 with the same volume v per molecule, and with a decrease in work function value. Under these conditions the system would be at equilibrium, and the derivative (equation 29) would be zero.

A theorem of M. E. Lemaire given in Borel's book on series of positive terms, translated into our nomenclature, states that

$$\text{minimum with respect to } x \text{ of } [a(x) - x \ln r_0 - (1 - x) \ln \rho_0] = 0$$

for any pair of associated radii of convergence r_0, ρ_0 .

Using equation 29 this may be rewritten as

$$a(x) = \begin{matrix} \text{maximum with} \\ \text{respect to } r_0 \text{ and} \\ \rho_0 \text{ at constant } x \end{matrix} \left[x \ln r_0 + \chi \ln \rho_0 \right] \quad (30)$$

where $\chi = 1 - x$, and the maximum must, of course, be taken subject to the equation determining the values r_0 and ρ_0 of the associated radii of convergence.

We now have the complete mathematical apparatus necessary to write the thermodynamical equations for the system. Using equations 26a and 26b

$$\begin{aligned} f(x, r_0, \rho_0) &= x \ln r_0 + \chi \ln \rho_0 \\ &= x \ln z + \chi \ln \zeta - v g_{0,0} \end{aligned} \quad (31)$$

in which the function f is defined by the first line of this equation. With equations 20a, 20b, and C-12 in terms of y and η ,

$$\begin{aligned} f(x, r_0, \rho_0) &= x \ln y + \chi \ln \eta - \frac{x}{y} G_{1,0} - \frac{\chi}{\eta} G_{0,1} - \\ &\quad v(y + \eta - G_{1,0} - G_{0,1} + G_{0,0}) \end{aligned} \quad (31')$$

The total differential of f , at constant mole fraction x , may be calculated for changes in z and ζ from equation 31, or for changes in y and η from equation 31', as

$$df = (x - v g_{1,0}) \frac{dz}{z} + (\chi - v g_{0,1}) \frac{d\zeta}{\zeta} \quad (32)$$

$$df = \left[\left(\frac{x}{y} - v \right) W - \left(\frac{\chi}{\eta} - v \right) w \right] \frac{dy}{y} - \left[\left(\frac{x}{y} - v \right) w - \left(\frac{\chi}{\eta} - v \right) \Omega \right] \frac{d\eta}{\eta} \quad (32')$$

An absolute maximum with respect to z and ζ is obtained if equations 14a and 14b are obeyed, and a corresponding maximum with respect to y and η if equations 21a and 21b are fulfilled. These equations (14a and 14b) or the corresponding pair (21a and 21b) show that this absolute maximum occurs at values of z, ζ and y, η which satisfy the conditions a and α , respectively.

These equations determine the values of z, ζ or of y, η for which $H(vb, r, \rho)$ diverges, and simultaneously for which $f(x, r_0, \rho_0)$ has its maximum value at the corresponding value of x and $\chi = 1 - x$. These values of z, ζ or of y, η , then, if inserted in equation 31 or 31' lead to values of f which are equal to $a(x)$.

Equation 13 and the subsequent equations of the previous section are thus proved, as long as the values of the variable pairs are smaller than those for which condition b or the equivalent conditions β or γ are obeyed.

IV. CONDENSATION

For sufficiently large volumes condition α must be fulfilled at smaller values of y and η than either condition β or condition γ . The equations thus obtained are those of the imperfect gas, which, at infinite volume, go over asymptotically to those of the perfect gas.

At given x and $\chi = 1 - x$, as the volume v is decreased there will be a certain volume, v_s , such that when

$$y_s = \frac{x}{v_s} \quad (33a)$$

$$\eta_s = \frac{\chi}{v_s} \quad (33b)$$

condition β or condition γ will be obeyed. Whether condition β or condition γ will be fulfilled will depend primarily on the temperature T , and to a less extent on x . In general, at low temperatures condition γ will determine the value of v_s . One must expect a temperature range at higher temperatures for which v_s is determined by the condition β .

This volume, v_s , is the volume per molecule of the saturated vapor with mole fraction x of component a . As the volume v is decreased below v_s , the values of the variables y and η to be used in the equations for the system will change, and in such a way as to continue to satisfy condition β or condition γ , as the case may be, and also to keep df of equation 32' equal to zero.

At any given volume $v < v_s$, the values of y and η so calculated determine the mole fractions x_s and χ_s of the saturated vapor in equilibrium with the

condensed phase present, as well as the volume per molecule, v_s , of the saturated vapor under the new equilibrium conditions. The equations are

$$v_s = \frac{1}{y + \eta}, \quad x_s = \frac{y}{y + \eta}, \quad \chi_s = \frac{\eta}{y + \eta} \quad (34)$$

V. CONCLUSION

The formal mathematical equations for the thermodynamical properties of a two-component system may be calculated, analogously to the case of a one-component system, in terms of certain integrals in the configuration space.

The general development of the thermodynamic functions of the imperfect gas with respect to inverse powers of the volume may be made in terms of the irreducible integrals $B_{k,\kappa}$ defined by equation 9. The equations, for the most important functions, are:

$$A = RT \left[x \ln \left(\frac{h^2}{2\pi m_a kT} \right)^{3/2} \frac{x}{ev} + \chi \ln \left(\frac{h^2}{2\pi m_\alpha kT} \right)^{3/2} \frac{\chi}{ev} - \sum_{k=0}^{\infty} \sum_{\kappa=0}^{\infty} B_{k,\kappa} x^k \chi^\kappa v^{-(k+\kappa-1)} \right] \quad (35)$$

$$F = RT \left[x \ln \left(\frac{h^2}{2\pi m_a kT} \right)^{3/2} \frac{x}{v} + \chi \ln \left(\frac{h^2}{2\pi m_\alpha kT} \right)^{3/2} \frac{\chi}{v} - \sum_{k=0}^{\infty} \sum_{\kappa=0}^{\infty} (k + \kappa) B_{k,\kappa} x^k \chi^\kappa v^{-(k+\kappa-1)} \right] \quad (36)$$

$$\mu_a = kT \left[\ln \left(\frac{h^2}{2\pi m_a kT} \right)^{3/2} \frac{x}{v} - \frac{1}{x} \sum_{k=0}^{\infty} \sum_{\kappa=0}^{\infty} k B_{k,\kappa} x^k \chi^\kappa v^{-(k+\kappa-1)} \right] \quad (37a)$$

$$\mu_\alpha = kT \left[\ln \left(\frac{h^2}{2\pi m_\alpha kT} \right)^{3/2} \frac{\chi}{v} - \frac{1}{\chi} \sum_{k=0}^{\infty} \sum_{\kappa=0}^{\infty} \kappa B_{k,\kappa} x^k \chi^\kappa v^{-(k+\kappa-1)} \right] \quad (37b)$$

$$P = \frac{kT}{v} \left[1 - \sum_{k=0}^{\infty} \sum_{\kappa=0}^{\infty} (k + \kappa - 1) B_{k,\kappa} x^k \chi^\kappa v^{-(k+\kappa-1)} \right] \quad (38)$$

$$v \left(\frac{\partial P}{\partial v} \right)_T = - \frac{kT}{v} \left[1 - \sum_{k=0}^{\infty} \sum_{\kappa=0}^{\infty} (k + \kappa)(k + \kappa - 1) B_{k,\kappa} x^k \chi^\kappa v^{-(k+\kappa-1)} \right] \quad (39)$$

where $B_{k,\kappa} = 0$ if $k + \kappa < 2$, and x and χ are the mole fractions of the components a and α , respectively.

The condition for condensation to begin is, at low temperatures, that the series of these equations become divergent. At higher temperatures the condition is that $W\Omega - w^2 = 0$, where the functions W , Ω , and w are defined in equations 27a, 27b, and 28.

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APPENDIX A: THE EVALUATION OF THE FUNCTION $H(vb, r, \rho)$

The configuration integral $Q_\tau(L, \Lambda, vb)$ for L molecules of type a and Λ molecules of type α , for a system in a volume $V = (L + \Lambda)v = Nv$, is given by equation 5. The sum in this equation is the coefficient of $z^L \zeta^\Lambda$ in the function $\exp(L + \Lambda)vg_{0,0}$, where the sums $g_{m,\mu}$ are defined as functions of $b_{l,\lambda}$, z , and ζ by equations 10a and 10b. The configuration integral may therefore be written as a Cauchy integral, namely,

$$\begin{aligned} \frac{Q_\tau(L, \Lambda, vb)}{L! \Lambda!} &= \sum_{m_{l,\lambda}} \prod_{l,\lambda} \frac{(Nvb_{l,\lambda})^{m_{l,\lambda}}}{m_{l,\lambda}!} \\ &\quad \sum_{l,m_{l,\lambda}} lm_{l,\lambda} = L \\ &\quad \sum_{\lambda,m_{l,\lambda}} \lambda m_{l,\lambda} = \Lambda \\ &= -\frac{1}{4\pi^2} \oint \oint \frac{e^{(L+\Lambda)vg_{0,0}}}{z^L \zeta^\Lambda} \frac{dz}{z} \frac{d\zeta}{\zeta} \end{aligned} \quad (\text{A-1})$$

where the path of integration over z must enclose the point $z = 0$, and that over ζ must enclose $\zeta = 0$.

We shall prove that the double sum

$$\begin{aligned} H(vb, r, \rho) &= \sum_{L=0}^{\infty} \sum_{\Lambda=0}^{\infty} \frac{Q_\tau(L, \Lambda, vb)}{L! \Lambda!} r^L \rho^\Lambda \\ &= \frac{1}{1 - v(g_{1,0} + g_{0,1})} \end{aligned} \quad (\text{A-2})$$

where the z and ζ occurring in the sums $g_{m,\mu}$ are special values of the integration variables in equation A-1 determined by the equations

$$r = ze^{-vg_{0,0}} \quad (\text{A-3a})$$

$$\rho = \zeta e^{-vg_{0,0}} \quad (\text{A-3b})$$

The method of proof follows closely that used by Born and Fuchs (2), and by Kahn and Uhlenbeck (4) in the case of only one molecular species, for which only one pair of variables, r and z , occurs.

With equation A-1 the sum (equation A-2) may be written

$$H(vb, r, \rho) = - \frac{1}{4\pi^2} \sum_{L=0}^{\infty} \sum_{\Lambda=0}^{\infty} \oint \oint \left(\frac{re^{v_{g00}}}{z} \right)^L \left(\frac{\rho e^{v_{g00}}}{\zeta} \right)^{\Lambda} \frac{dz}{z} \frac{d\zeta}{\zeta} \quad (\text{A-4})$$

The integrations must be made over paths enclosing $z = 0$ and $\zeta = 0$, respectively, and no further singularities. In particular one can choose paths such that

$$| (r/z)e^{v_{g00}} | < 1 \quad (\text{A-5a})$$

$$| (\rho/\zeta)e^{v_{g00}} | < 1 \quad (\text{A-5b})$$

just as in the case of the single variable. In this case the order of summation and integration may be reversed, so that one obtains

$$H(vb, r, \rho) = - \frac{1}{4\pi^2} \oint \oint \frac{1}{z - re^{v_{g00}}} \frac{1}{\zeta - \rho e^{v_{g00}}} dz d\zeta \quad (\text{A-6})$$

Integrating, now, first over z , subject to condition A-5a, with fixed value of ζ , a pole enclosed by the path of integration is found when equation A-3a is satisfied. The pole when equation A-3b is obeyed is *not* enclosed by the path of integration over z .

Inserting the derivative of the denominator for the denominator at the pole, in order to evaluate the residue, one finds

$$H(vb, r, \rho) = \frac{1}{2\pi i} \oint \frac{1}{1 - vg_{1,0}} \frac{1}{\zeta - \rho e^{v_{g0,0}}} d\zeta \quad (\text{A-7})$$

where now the variable z occurring in $g_{1,0}$ and in $g_{0,0}$ has the special value determined by equation A-3a in terms of r and ρ .

Integrating now over ζ , subject to the condition A-5b, the pole when condition A-3b is satisfied is enclosed by the path of integration. The residue is determined as before by inserting the derivative of the denominator for the denominator at the pole. The derivative is to be taken with respect to ζ at the value of ζ determined by equation A-3b with fixed value of r . One finds that

$$\begin{aligned} \left(\frac{\partial}{\partial \zeta} \right)_r (\zeta - \rho e^{v_{g0,0}}) & \text{(at } \zeta \text{ determined by equation A-3b)} \\ &= 1 - v\zeta \left(\frac{\partial g_{0,0}}{\partial \zeta} \right)_z - v\zeta \left(\frac{\partial g_{0,0}}{\partial z} \right)_\zeta \frac{\zeta}{z} \left(\frac{\partial z}{\partial \zeta} \right)_r \\ &= 1 - vg_{0,1} - vg_{1,0} \frac{\zeta}{z} \left(\frac{\partial z}{\partial \zeta} \right)_r \end{aligned} \quad (\text{A-8})$$

From equation A-3a one may write

$$\frac{dr}{r} = (1 - vg_{1,0}) \frac{dz}{z} - vg_{0,1} \frac{d\zeta}{\zeta} \quad (\text{A-9})$$

so that, for $dr = 0$,

$$\left(\frac{\partial z}{\partial \zeta}\right)_r = \frac{z}{\zeta} \frac{vg_{0,1}}{1 - vg_{1,0}} \quad (\text{A-10})$$

Using equation A-10 in equation A-8, one obtains

$$\left(\frac{\partial}{\partial \zeta}\right)_r (\zeta - \rho e^{vg_{0,0}}) = 1 - vg_{0,1} - vg_{1,0} \frac{vg_{0,1}}{1 - vg_{1,0}} \quad (\text{A-11})$$

Finally, noting that

$$(1 - vg_{1,0})(1 - vg_{0,1}) - v^2 g_{1,0} g_{0,1} = 1 - v(g_{1,0} + g_{0,1}) \quad (\text{A-12})$$

the result (equation A-2) is obtained for $H(vb, r, \rho)$, where z and ζ are given by equations A-3a and A-3b. This proves equation A-2, provided that the paths of integration can be chosen subject to equations A-5a and A-5b so that only one pole each corresponding to equations A-3a and A-3b is enclosed by the respective path of integration. The argument showing this is an obvious extension of the argument given by Born and Fuchs (2) for the case of the single variable, and will not be repeated here.

APPENDIX B: THE CALCULATION OF THE COEFFICIENT OF THE PRODUCT $\prod B_{k,\kappa}^{n_{k,\kappa}}$ IN THE CLUSTER INTEGRAL $b_{l,\lambda}$

We wish to calculate the coefficient of the product

$$\prod_{k,\kappa} B_{k,\kappa}^{n_{k,\kappa}} \quad (\text{B-1})$$

in the cluster integral $b_{l,\lambda}$. It is to be remembered that $l! \lambda!$ occurs in the denominator of the definition (equation 8) of $b_{l,\lambda}$, and $k! \kappa!$ in the denominator of the definition (equation 9) of $B_{k,\kappa}$. The coefficient sought is therefore $(\Omega_s / l! \lambda!) \prod_{k,\kappa} (k! \kappa!)^{n_{k,\kappa}}$, if Ω_s is the number of ways in which diagrams may be drawn with l molecules of type a and λ molecules of type α , which correspond to the product B-1 for a given set s of the numbers $n_{k,\kappa}$.

The calculation of this number, Ω_s , is equivalent to the following problem: Suppose we are given l numbered round bolts, λ numbered square bolts, and $n_{k,\kappa}$ identical and unnumbered frames, each having k round and κ square holes symmetrically situated with respect to each other, for all values of k, κ subject to

$$\sum (k + \kappa - 1)n_{k,\kappa} = l + \lambda - 1 \quad (\text{B-2})$$

$$l \leq \sum k n_{k,\kappa} \leq l - 1 + \sum n_{k,\kappa} - \sum_{\kappa} n_{0,\kappa} \quad (\text{B-3a})$$

$$\lambda \leq \sum \kappa n_{k,\kappa} \leq \lambda - 1 + \sum n_{k,\kappa} - \sum_k n_{k,0} \quad (\text{B-3b})$$

where all undesigned sums run over both k and κ from zero on up. The quantity Ω_b is then the number of ways in which the bolts can be inserted so as to fill all the holes in the frames, bolting the frames together so as to form one singly connected complex.

The singly connected, or "bolted," arrangement of frames will have $\sum n_{k,\kappa} - 1$ "joining places" between frames, of which $n = \sum \kappa n_{k,\kappa} - l$ will be at round bolts, and $\nu = \sum \kappa n_{k,\kappa} - \lambda$ at square bolts. With equations B-3a and B-3b one then has

$$\sum n_{k,\kappa} - \sum_{\kappa} n_{0,\kappa} - 1 \geq n = \sum \kappa n_{k,\kappa} - l \geq 0 \quad (\text{B-4a})$$

$$\sum n_{k,\kappa} - \sum_k n_{k,0} - 1 \geq \nu = \sum \kappa n_{k,\kappa} - \lambda \geq 0 \quad (\text{B-4b})$$

To aid in the subsequent description we shall assume that at every joining place between two frames made with a round bolt there is necessarily inserted a round washer, and that at every joining place with a square bolt there is a square washer, so that the total number of round washers is n and of square washers is ν .

Now every "bolted arrangement" can be unbolted into a "dissociated arrangement" consisting of one free bolt and of all the unconnected frames, each with exactly one hole unfilled with a bolt. Any of the $l + \lambda$ bolts in the bolted arrangement may be selected as the free bolt, after which the unbolting process is uniquely determined. Since no two dissociated arrangements with differing free bolts are identical, it follows that each bolted arrangement may be formed by bolting together any of $l + \lambda$ different dissociated arrangements, l with a free round bolt, and λ with a free square bolt.

The number Ω_b of bolted arrangements which can be formed may then be calculated as: *either* the total number of dissociated arrangements divided by $l + \lambda$ and multiplied by the number of ways in which they can be bolted together; *or*, as the number of dissociated arrangements with a round bolt as the free bolt, divided by l , and multiplied by the number of ways of bolting together; *or*, as the number of dissociated arrangements with a free square bolt, divided by λ and multiplied by the number of ways of bolting together. We shall calculate with the second method, using a free round bolt.

In the dissociated arrangement it is necessary to distinguish between frames for which the free hole is round, and those for which it is square. We shall designate the number of frames with $k - 1$ round bolts, κ square bolts, and a free round hole by $m_{k,\kappa}$; and by $\mu_{k,\kappa}$ the number of frames with k round bolts, $\kappa - 1$ square bolts, and a free square hole. We have then, that

$$m_{k,\kappa} + \mu_{k,\kappa} = n_{k,\kappa} \quad (\text{B-5})$$

In a dissociated arrangement with a free *round* bolt, one has that

$$\sum m_{k,\kappa} = n + 1 \quad (\text{B-6a})$$

$$\sum \mu_{k,\kappa} = \nu \quad (\text{B-6b})$$

With a given set of the numbers $m_{k,\kappa}$ and $\mu_{k,\kappa}$, the total number of dissociated arrangements which can be made may be readily calculated as the number of ways in which the l numbered round bolts and the λ numbered square bolts may be distributed among the unnumbered frames, and is

$$l! \lambda! \prod_{k,\kappa} \frac{1}{(k! \kappa!)^{n_{k,\kappa}}} \frac{k^{m_{k,\kappa}} \kappa^{\mu_{k,\kappa}}}{m_{k,\kappa}! \mu_{k,\kappa}!} \quad (\text{B-7})$$

The quantity in B-7 must be divided by l and multiplied by the number of ways in which the dissociated arrangement can be bolted together, and then summed for all values of $m_{k,\kappa}$ and $\mu_{k,\kappa}$ subject to B-5, B-6a, B-6b, in order to obtain Ω_s .

It is necessary now to calculate the number of ways in which the dissociated arrangement can be bolted together to give bolted arrangements.

Consider, in a definite dissociated arrangement, that a definite assignment of washers to the bolts has been made, so that the numbers f_m of round washers on each round bolt m , and the numbers ϕ_μ of square washers on each square bolt μ , are given. Suppose that, of the ν square washers the number ν_a are in frames with a free square hole, and the number ν_s are in frames with a round free hole.

With this assignment of the washers to the bolts we shall prove that the number of ways in which the dissociated arrangement can be bolted together is

$$\frac{\nu_a}{\nu} \prod_{\mu} \frac{\nu!}{\phi_\mu!} \prod_m \frac{n!}{f_m!} \quad (\text{B-8})$$

The proof follows: We select a square bolt in a frame with a square free hole, having, say, ϕ_1 washers assigned to it. This is to be bolted to ϕ_1 of the $\nu - 1$ frames other than its own which have square free holes. The bolting can be done in

$$\frac{(\nu - 1)!}{(\nu - \phi_1 - 1)! \phi_1!}$$

different ways, since the order of bolting is immaterial. The complex of $\phi_1 + 1$ frames which is so formed has exactly one square hole and behaves, for the remaining process, exactly like a frame with a square hole. The total number of frames with square holes has been decreased by this process from ν to $\nu - \phi_1$. Repeating until all ν_a square washers which were

in frames of square free holes have been used, we find that they can be bolted in

$$\frac{(\nu - 1)!}{(\nu - 1 - \nu_a)!} \prod_{\mu} \phi_{\mu}! \quad (\text{B-9})$$

different ways, where $\prod_{\mu} \phi_{\mu}!$ goes, of course, only over the ϕ values of the square bolts in frames with free square holes.

There now remain $\nu - \nu_a = \nu_a$ complexes or frames with square holes. It is also seen from B-9 that unless $\nu_a \geq 1$ we will have gotten into trouble with the last washer, which would have had no frame to which it could have been bolted.

Continuing now with the square bolts in frames with free round holes, we find that any selected bolt with, say, ϕ_2 washers, may be bolted in

$$\frac{(\nu - \nu_a)!}{(\nu - \nu_a - \phi_2)! \phi_2!} = \frac{\nu_a(\nu - \nu_a - 1)!}{(\nu - \nu_a - \phi_2)! \phi_2!}$$

ways to any ϕ_2 of the remaining ν_a frames or complexes with square holes free. Repeating until all the square washers have been used, one finds that the square bolts can be used to bolt the frames together into incomplete complexes in

$$\nu_a \frac{(\nu - 1)!}{\prod_{\mu} \phi_{\mu}!} = \frac{\nu_a}{\nu} \frac{\nu!}{\prod_{\mu} \phi_{\mu}!} \quad (\text{B-10})$$

different ways.

There remain now $n + 1$ complexes or frames, each with one round hole, and with n round washers altogether, and also one free round bolt.

Again we select some bolt, this time a round one with, say, f_1 washers. This can be bolted to f_1 of the n frames other than its own in

$$\frac{n!}{(n - f_1)! f_1!}$$

different ways. If the free bolt is chosen last in the bolting process one gets into no difficulties, and the number of ways in which the round bolts may be used to bolt the complexes and frames together so as to end with a completely bolted arrangement is

$$\frac{n!}{\prod_m f_m!} \quad (\text{B-11})$$

Multiplication of B-10 by B-11 leads to B-8 as the number of ways in which the dissociated arrangement may be bolted together with a given

assignment of the washers to the bolts, that is, with a given set of the numbers f_m and ϕ_μ .

Now a given set of the numbers f_m and ϕ_μ of washers on each bolt m and μ can be formed in

$$\frac{\nu!}{\prod_{\mu} \phi_{\mu}!} \frac{n!}{\prod_m f_m!}$$

different ways if the washers are numbered, so from expressions B-8 and B-12 it is seen that the number of ways in which the dissociated arrangements can be bolted together is ν_a/ν times the number of ways in which the numbered washers can be assigned to the bolts consistent with a given ν_a , and summed over all values of ν_a from unity to ν .

The number of ways in which, of the ν numbered square washers, ν_a can be assigned to any of the $\sum \kappa m_{k,\kappa}$ numbered square bolts in frames with a free round hole, and $\nu_a = \nu - \nu_a$ to the $\lambda - \sum \kappa m_{k,\kappa}$ square bolts in frames with a free square hole is

$$\frac{\nu!}{\nu_a! (\nu - \nu_a)!} (\sum \kappa m_{k,\kappa})^{\nu_a} (\lambda - \sum \kappa m_{k,\kappa})^{(\nu - \nu_a)} \quad (\text{B-13})$$

Multiplication of expression B-13 by ν_a/ν and summing over all values of ν_a from 1 to ν leads to

$$\lambda^{(\nu-1)} \sum \kappa m_{k\kappa} \quad (\text{B-14})$$

The number of ways that the n numbered round washers can be assigned to the l round bolts is

$$l^n \quad (\text{B-15})$$

Multiplying B-13 by B-14 gives the number of ways in which the dissociated arrangements can be bolted together as

$$l^n \lambda^{(\nu-1)} \sum \kappa m_{k,\kappa} \quad (\text{B-16})$$

Finally, B-7 multiplied by B-16 and divided by l gives the equation for Ω_s as

$$\Omega_s = \frac{l! \lambda!}{l^2 \lambda} \sum_{\substack{m_{k\kappa} \\ \mu_{k\kappa}}} \prod_{k,\kappa} \frac{(lk)^{m_{k\kappa}} (\lambda \kappa)^{\mu_{k\kappa}} \sum \kappa m_{k,\kappa}}{(k! \kappa!)^{m_{k,\kappa} + \mu_{k,\kappa}} m_{k,\kappa}! \mu_{k,\kappa}!} \quad (\text{B-17})$$

in which the summation over $m_{k,\kappa}$ and $\mu_{k,\kappa}$ is subject to the conditions determined by equations B-4 to B-6 inclusive. These may be rewritten as

$$\sum m_{k,\kappa} = \sum k(m_{k,\kappa} + \mu_{k,\kappa} - l + 1) \geq 0 \quad (\text{B-18a})$$

$$\sum \mu_{k,\kappa} = \sum \kappa(m_{k,\kappa} + \mu_{k,\kappa}) - \lambda \geq 0 \quad (\text{B-18b})$$

The upper limits on the sums, $\sum m_{k,\kappa}$ and $\sum \mu_{k,\kappa}$ finally reduce merely to the requirement that $\sum \kappa m_{k,\kappa}$ be greater than zero, and since equation B-17 contains this sum as a factor these limits may be omitted.

Finally, multiplication of Ω_s by $\prod_{k,\kappa} (k!\kappa!)^{n_{k,\kappa}}/l!\lambda!$ to obtain the coefficient in $b_{l,\lambda}$ leads to the equation for $b_{l,\lambda}$,

$$l^2 \lambda b_{l,\lambda} = \sum_{m_{k,\kappa}, \mu_{k,\kappa}} \prod_{k,\kappa} \frac{(lk)^{m_{k,\kappa}} (\lambda \kappa)^{\mu_{k,\kappa}}}{m_{k,\kappa}! \mu_{k,\kappa}!} \left(\sum \kappa m_{k,\kappa} \right) B_{k,\kappa}^{m_{k,\kappa} + \mu_{k,\kappa}} \quad (\text{B-19})$$

in which the summation is subject to the limitations of equations B-18a and B-18b.

Equation B-19 is not obviously symmetrical in l and λ , which, in view of its derivation by considering only the dissociated arrangements with free round bolts, should be checked. It is also not in a convenient form for the purposes of calculation. We shall now proceed to alter its form by expressing $l\lambda b_{l,\lambda}$ as a Cauchy integral, in which form it can be seen that the expression is completely symmetrical in the two kinds of molecules.

The sum on the right-hand side of equation B-19 is seen to be the coefficient $y^{l-1} \eta^\lambda$ in the development of the function

$$e^{\lambda \sigma_{01}/\eta} \eta \frac{\partial}{\partial \eta} e^{l \sigma_{10}/y} \quad (\text{B-20})$$

where the sums $(\sigma'_{0,1})$ and $(\sigma'_{1,0})$, which are functions of $B_{k,\kappa}$ and of y and η are defined in equation 20-b. The equality of the coefficient of $y^{l-1} \eta^\lambda$ in equation B-20 with the expression B-19 can most easily be seen by direct development of the function B-20

$$\begin{aligned} e^{\lambda \sigma_{01}/\eta} \eta \frac{\partial}{\partial \eta} e^{l \sigma_{10}/y} &= \sum_{\mu_{k,\kappa}} \prod_{k,\kappa} \frac{(\lambda \kappa)^{\mu_{k,\kappa}}}{\mu_{k,\kappa}!} B_{k,\kappa}^{\mu_{k,\kappa}} y^{k \mu_{k,\kappa}} \eta^{(\kappa-1) \mu_{k,\kappa}} \eta \frac{\partial}{\partial \eta} \sum_{m_{k,\kappa}} \prod_{k,\kappa} \frac{(lk)^{m_{k,\kappa}}}{m_{k,\kappa}!} B_{k,\kappa}^{m_{k,\kappa}} y^{(k-1) m_{k,\kappa}} \eta^{m_{k,\kappa}} \\ &= \sum_{\substack{m_{k,\kappa} \\ \mu_{k,\kappa}}} \prod_{k,\kappa} \frac{(lk)^{m_{k,\kappa}} (\lambda \kappa)^{\mu_{k,\kappa}}}{m_{k,\kappa}! \mu_{k,\kappa}!} \left(\sum \kappa m_{k,\kappa} \right) B_{k,\kappa}^{(m_{k,\kappa} + \mu_{k,\kappa})} y^{k(m_{k,\kappa} + \mu_{k,\kappa}) - m_{k,\kappa}} \eta^{\kappa(m_{k,\kappa} + \mu_{k,\kappa}) - \mu_{k,\kappa}} \end{aligned} \quad (\text{B-20}')$$

If now the indicated differentiation is carried out in the original form for the function B-20, one obtains

$$e^{\lambda \sigma_{01}/\eta} \eta \frac{\partial}{\partial \eta} e^{l \sigma_{10}/y} = \frac{l}{y} G_{1,1} e^{l \sigma_{10}/y} e^{\lambda \sigma_{01}/\eta} \quad (\text{B-21})$$

From this one obtains the equation, symmetrical in l and λ , that $l\lambda b_{l,\lambda}$ is the coefficient of $y^l \eta^\lambda$ in

$$G_{1,1} e^{l \sigma_{10}/y} e^{\lambda \sigma_{01}/\eta}$$

With the use of the Cauchy integral one may write

$$\lambda b_{l,\lambda} = -\frac{1}{4\pi^2} \oint \oint G_{1,1} e^{i\sigma_{10}/y} e^{\lambda\sigma_{01}/\eta} \frac{dy}{y^{l+1}} \frac{d\eta}{\eta^{\lambda+1}} \quad (\text{B-23})$$

where the path of integration of y must enclose the point $y = 0$, and the path of integration of η enclose $\eta = 0$. The form (equation B-23) for $\lambda b_{l,\lambda}$ will be used in appendix C for the calculation of the sum $g_{1,1}$.

APPENDIX C: THE EVALUATION OF THE FUNCTIONS $g_{m,\mu}$

With equation B-23 for $\lambda b_{l,\lambda}$ the evaluation of the sum

$$\begin{aligned} g_{1,1} &= \sum_{l=0}^{\infty} \sum_{\lambda=0}^{\infty} \lambda b_{l,\lambda} z^l \zeta^\lambda \\ &= -\frac{1}{4\pi^2} \sum_{l=0}^{\infty} \sum_{\lambda=0}^{\infty} \oint \oint G_{1,1} \left(\frac{ze^{\sigma_{10}/y}}{y} \right)^l \left(\frac{\zeta e^{\sigma_{01}/\eta}}{\eta} \right)^\lambda \frac{dy}{y} \frac{d\eta}{\eta} \end{aligned} \quad (\text{C-1})$$

follows practically the same method as that used for $H(vb, r, \rho)$ in appendix A. By limiting ourselves to integration paths for which

$$|(z/y)e^{\sigma_{10}/y}| < 1 \quad (\text{C-2a})$$

$$|(\zeta/\eta)e^{\sigma_{01}/\eta}| < 1 \quad (\text{C-2b})$$

the order of summation and integration may be reversed, obtaining

$$g_{1,1} = -\frac{1}{4\pi^2} \oint \oint G_{1,1} \frac{1}{y - ze^{\sigma_{10}/y}} \frac{1}{\eta - \zeta e^{\sigma_{01}/\eta}} dy d\eta \quad (\text{C-3})$$

Integrating this first over y , the pole

$$z = ye^{-\sigma_{10}/y} \quad (\text{C-4a})$$

is enclosed by the path of integration and the residue evaluated by taking the derivative of the denominator at the pole. One obtains

$$\begin{aligned} g_{1,1} &= \frac{1}{2\pi i} \oint G_{1,1} \frac{y}{(y - G_{2,0} + G_{1,0})} \frac{1}{\eta - \zeta e^{\sigma_{01}/\eta}} d\eta \\ &= \frac{1}{2\pi i} \oint \frac{yw}{W} \frac{1}{\eta - \zeta e^{\sigma_{01}/\eta}} d\eta \end{aligned} \quad (\text{C-5})$$

where the functions W and w are defined, with their companion Ω , by equations 27a, 27b, and 28. The value of y to be used in equation C-5 is that of equation C-4a.

Integrating now over η , the pole at

$$\zeta = \eta e^{-\sigma_{01}/\eta} \quad (\text{C-4b})$$

is enclosed by the path of integration. The derivative of the denominator with respect to η at the pole must be taken with constant z . One finds that

$$\left(\frac{\partial}{\partial \eta}\right)_z (\eta - \zeta e^{\sigma_{01}/\eta}) = \frac{1}{\eta} \left[\Omega - w \frac{\eta}{y} \left(\frac{\partial y}{\partial \eta}\right)_z \right] \quad (\text{C-6})$$

From equation C-4a

$$\frac{dz}{z} = \frac{1}{y} \left[W \frac{dy}{y} - w \frac{d\eta}{\eta} \right] \quad (\text{C-7a})$$

so that, with $dz = 0$,

$$\frac{\eta}{y} \left(\frac{\partial y}{\partial \eta}\right)_z = \frac{w}{W} \quad (\text{C-8a})$$

is obtained. Using this, equation C-6 is found to be

$$\left(\frac{\partial}{\partial \eta}\right)_z (\eta - \zeta e^{\sigma_{01}/\eta}) = \frac{1}{\eta} \left(\Omega - \frac{w^2}{W} \right) \quad (\text{C-9})$$

and the function $g_{1,1}$ is then given as

$$g_{1,1} = \frac{y\eta w}{W\Omega - w^2} \quad (\text{C-10})$$

where the values of y and η are determined by equations C-4a and C-4b.

The relationships between the various sums $g_{m,\mu}$ are given in equation 31a.

If the companion equations to equations C-7a and C-8a,

$$\frac{d\zeta}{\zeta} = \frac{1}{\eta} \left[\Omega \frac{d\eta}{\eta} - w \frac{dy}{y} \right] \quad (\text{C-7b})$$

$$\frac{y}{\eta} \left(\frac{\partial \eta}{\partial y}\right)_\zeta = \frac{w}{\Omega} \quad (\text{C-8b})$$

are used, one finds that

$$\frac{z}{y} \left(\frac{\partial y}{\partial z}\right)_\zeta = \frac{y\Omega}{W\Omega - w^2} \quad (\text{C-11a})$$

$$\frac{\zeta}{\eta} \left(\frac{\partial \eta}{\partial \zeta}\right)_z = \frac{\eta W}{W\Omega - w^2} \quad (\text{C-11-b})$$

$$z \left(\frac{\partial \eta}{\partial z}\right)_\zeta = \zeta \left(\frac{\partial y}{\partial \zeta}\right)_z = \frac{y\eta w}{W\Omega - w^2} \quad (\text{C-11c})$$

With these equations, and the relationship 11a, direct differentiation of the expressions

$$g_{0,0} = y + \eta - G_{1,0} - G_{0,1} + G_{0,0} \quad (\text{C-12})$$

$$g_{1,0} = y \quad (\text{C-13a})$$

$$g_{0,1} = \eta \quad (\text{C-13b})$$

to obtain $g_{1,1}$ shows that the set of equations above is correct to within constants of integration which depend only on y or only on η . That these "constants" have been correctly chosen follows from the fact that by setting either $z = 0$ and $y = 0$, or by setting $\zeta = 0$ and $\eta = 0$, the above equations reduce correctly to those for the case of a gas composed of one component molecular type only, equations which have been reported in previous papers (2, 7).

This simple algebraic checking will be omitted here, but it may be well to point out that, owing to the difference in normalization, the irreducible integral $B_{k,0}$ corresponds to β_{k-1}/k in the old notation. It follows that the sum $G_{1,0}$, which is zero if $y = 0$, reduces to $g_0(\beta, y)$ in the old notation when $\eta = 0$.

APPENDIX D: THE CONDITION THAT $H(vb, r, \rho)$ IS SINGULAR

The values of the three complex variable pairs $(r, \rho; z, \zeta; \text{ and } y, \eta)$ for which the function $H(vb, r, \rho)$ is singular, are values of particular significance.

One fact, which is sufficient for our purposes, that the coefficients $Q\tau(L, \Lambda, vb)/L! \Lambda!$ of $r^L \rho^\Lambda$ in H are all real and positive, is of great importance. From this it follows that the first singularity of H , determining associated radii r_0 and ρ_0 of the circles of convergence, occurs on the real positive axes of r and ρ , and also that for positive values of r and ρ the function H itself is always positive.

It is clear that H is regular for all values of z and ζ such that both

$$(a) \quad g_{1,0} + g_{0,1} \neq \frac{1}{v}$$

and

$$(b) \quad g_{1,0} + g_{0,1} \text{ regular}$$

are obeyed.

Further it is evident from conditions a and b that H is regular if all three conditions

$$(\alpha) \quad y + \eta \neq \frac{1}{v}$$

$$(\beta) \quad W\Omega - w^2 \neq 0$$

$$(\gamma) \quad \text{All } G_{m,\mu} \text{ regular}$$

are obeyed for the functions of y and η .

We shall prove that the first singularity of H occurs when any of the conditions a , b or α , β , γ are violated on the real positive axes of the variable pairs z, ζ or y, η .

From equation A-2 it is seen that H is singular whenever condition a is violated, and from equations 13a and 13b that condition α is equivalent to condition a .

From the relations (11a) connecting the functions $g_{m,\mu}$ it is seen that $g_{1,0} + g_{0,1}$ is singular whenever either $g_{0,0}$ or $g_{1,1}$ is singular. Similarly, from relation 11b, whenever any of the sums $G_{m,\mu}$ is singular, the sum $G_{1,0} + G_{0,1} - G_{0,0}$ is singular.

From equation C-10 one sees that whenever condition β is violated, condition b is also.

The Jacobian $\partial(y, \eta)/\partial(z, \zeta)$ may be calculated from the equations C-11 to be

$$\begin{vmatrix} \frac{\partial y}{\partial z} & \frac{\partial y}{\partial \zeta} \\ \frac{\partial \eta}{\partial z} & \frac{\partial \eta}{\partial \zeta} \end{vmatrix} = \frac{y^2 \eta^2}{z \zeta} \quad (\text{D-1})$$

The corresponding Jacobian for z, ζ and r, ρ may be calculated to be

$$\begin{vmatrix} \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \rho} \\ \frac{\partial \zeta}{\partial r} & \frac{\partial \zeta}{\partial \rho} \end{vmatrix} = \frac{z \zeta}{r \rho} \quad (\text{D-2})$$

Neither of these functions is singular or zero.

Consider a "thin" region in the four-dimensional space of the two complex variables r and ρ which consists of all those pairs of r and ρ for which the real parts lie between zero and the line of nearest singularities of H , while the imaginary parts are small in absolute value. This thin four-dimensional region is mapped by the composite of transformations A-3a and A-3b in a one-to-one manner on a region of the complex (z, ζ) -space in such a way that positive values of r and ρ correspond to positive values of z and ζ .

This region of the (z, ζ) -space, in turn, is similarly mapped on a region of the (y, η) -space.

In view of the non-vanishing of the Jacobians of the component map-

pings, the composed mapping cannot create or destroy a singularity within the image of these regions.

From equation A-2 it is seen that H is zero if $g_{1,0} + g_{0,1}$ becomes infinite. H cannot be zero for real positive r and ρ , so that this possibility is excluded. If $g_{1,0} + g_{0,1}$ has an essential singularity, H must be singular in view of the non-vanishing Jacobian. It therefore follows that if condition b is violated on the real positive axes of z and ζ , the function H is singular.

From equation C-12 and the non-vanishing of the Jacobian D-1, it is seen that $g_{0,0}$ and therefore $g_{1,0} + g_{0,1}$ are singular if $G_{1,0} + G_{0,1} - G_{0,0}$ is singular. It follows that H is singular if condition γ is violated on the real positive axes of y and η .

NOTATION

$A = E - TS$, work function, or Helmholtz free energy.

a and α are used as subscripts to indicate molecules of type a or of type α .

$$a(x) = \frac{1}{RT} \left[A(x) - \ln \left(\frac{h^2}{2\pi m_a kT} \right)^{3x/2} \left(\frac{h^2}{2\pi m_\alpha kT} \right)^{3\chi/2} \right]$$

$$= \lim_{ND_x \rightarrow \infty} \left[-\frac{1}{ND_x \chi} \ln \frac{Q_r(ND_x \chi, ND_x(1-x), vb)}{ND_x x! ND(1-x)!} \right]$$

$B_{k,\kappa}$ = irreducible integral of k molecules of type a and of κ molecules of type α (defined in equation 9).

$b_{l,\lambda}$ = cluster integral of l molecules of type a , λ molecules of type α (defined in equation 8).

D_x = irreducible denominator of rational x .

$F = A + PV = E + PV - TS$, Gibbs' free energy.

$f(x, r_0, \rho_0) = x \ln r_0 - \chi \ln \rho_0$.

$$G_{m,\mu} = \sum_{k=0}^{\infty} \sum_{\kappa=0}^{\infty} k^m \kappa^\mu B_{k,\kappa} y^k \eta^\kappa, \quad (B_{k,\kappa} = 0 \text{ if } k + \kappa < 2).$$

$$g_{m,\mu} = \sum_{l=0}^{\infty} \sum_{\lambda=0}^{\infty} l^m \lambda^\mu b_{l,\lambda} z^l \zeta^\lambda, \quad (b_{0,0} = 0).$$

$$H(vb, r, \rho) = \sum_{L=0}^{\infty} \sum_{\Lambda=0}^{\infty} \frac{Q_r(L, \Lambda, vb)}{L! \Lambda!} r^L \rho^\Lambda, \quad (Q_r(0, 0, vb) = 1).$$

L, Λ = total number of molecules of types a and α , respectively, in the system.

$N = L + \Lambda$, total number of molecules in the system.

Q = phase integral.

$Q_r(L, \Lambda, vb)$ = configuration integral, the volume-dependent factor of Q multiplied by $L! \Lambda!$.

r, ρ = variables of $H(vb, r, \rho)$.

r_0, ρ_0 = radii of convergence of $H(vb, r, \rho)$, related to the work function per molecule.

$v = V/N$, volume per molecule in the system.

v_s = volume per molecule in the saturated vapor.

$W = (y - G_{2,0} + G_{1,0})$.

$\Omega = (\eta - G_{0,2} + G_{0,1})$.

$w = G_{1,1}$.

$x, \chi = L/N$ and Λ/N , respectively, the mole fractions of molecules of types a and α , respectively, in the system.

x_s, χ_s = the mole fractions of a and α , respectively, in the saturated vapor.

y and η are used in three senses: (I) as variables in a Cauchy integral; (II) as special values of these variables for which the integrand has a pole, thus they appear in the integrated expression of the integral; (III) as a special case of II, for which the other parameters of the integral have such values that $H(vb, r, \rho)$ diverges. In this last case they are numerically x/v and χ/v , respectively, if the system is one phase gaseous, or x_s/v_s and χ_s/v_s , respectively, if a liquid phase is present.

z and ζ are used in three senses: (I) as variables of integration in a Cauchy integral; (II) as special values of these for which the integrand has a singularity in the expression for the integrated Cauchy integral; (III) as a special case of II for which the parameters of the integral have such a value that $H(vb, r, \rho)$ diverges. In this case they are related to the chemical potentials μ_a and μ_α , respectively, by equations 19a and 19b.

REFERENCES

- (1) BORN, MAX: *Physica* **4**, 1034 (1937).
- (2) BORN, MAX, AND FUCHS, KLAUS: *Proc. Roy. Soc. (London)* **A166**, 391 (1938).
- (3) HARRISON, S. F., AND MAYER, JOSEPH E.: *J. Chem. Phys.* **6**, 107 (1938).
- (4) KAHN, B., AND UHLENBECK, G. E.: *Physica* **5**, 399 (1938).
- (5) MAYER, JOSEPH E.: *J. Chem. Phys.* **5**, 67 (1937).
- (6) MAYER, JOSEPH E., AND ACKERMANN, PHILIP G.: *J. Chem. Phys.* **5**, 74 (1937).
- (7) MAYER, JOSEPH E. AND HARRISON, S. F.: *J. Chem. Phys.* **6**, 87 (1938).
- (8) URSELL, H. D.: *Proc. Cambridge Phil. Soc.* **23**, 685 (1927).

ORDER AND DISORDER IN LIQUID SOLUTIONS¹

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I

A large number of non-polar liquid mixtures conform approximately to the laws of the regular solution, originally formulated by Hildebrand (3) on the basis of thermodynamic considerations. The regular solution has been treated from a molecular point of view by Scatchard (7), by Hildebrand and Wood (4), and by Guggenheim (2). A regular solution is primarily characterized by the fact that it possesses the entropy of mixing of an ideal solution. This implies the existence of a random molecular distribution in the solution. By random distribution we mean that the neighbors of each molecule are, on the average, distributed among the various molecular species of the mixture in the proportion of their mole fractions, the average local composition in the vicinity of the molecule being identical with the bulk composition of the solution. In real solutions with non-vanishing heats of mixing, random distribution can scarcely provide more than an approximate description of the actual situation. In seeking an explanation for the departure of actual solutions from regular behavior, it is therefore of importance to study the influence of deviations from random distribution on the thermodynamic functions of the system. The present investigation is concerned with this problem.

The average distribution of the neighbors of a molecule in solution, among the various molecular species present, is determined by two opposing influences,—the disordering effect of thermal motion and the ordering effect of intermolecular forces. For example, in a binary solution in which the intermolecular attraction between unlike molecules is greater than that between like molecules, each molecule will exert an ordering influence in its vicinity resulting in a local composition richer in molecules of the opposite species than the solution in bulk. On the other hand, if the attraction between like molecules is greater than between unlike, a local composition in the vicinity of each molecule, richer in molecules of the same species, will result. The extent to which local segregation of this

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sort can be established depends upon the violence of thermal motion and will be greater the lower the temperature. At sufficiently low temperatures it may manifest itself on a macroscopic scale by causing the solution to separate into two phases.

The problem of local order or order of neighbors was discussed by Bethe (1) from a quantitative point of view in his theory of superlattices in solid solutions. Into this problem there entered another type of order, long-range order, relating to the segregation of the components on interpenetrating lattices in the crystal. Since there can be no question of the establishment of long-range order in liquid solutions, we need only concern ourselves with local order. An alternative method of treating order and disorder in solid solutions, developed by the writer (5), is particularly well adapted to the investigation of local order in liquid solutions. Although, in the meantime, the problem has been treated by Rushbrooke (6), using Bethe's method, it seems worthwhile to discuss the question from the standpoint of our method if only because of its simplicity and directness.

II

We consider a non-polar binary liquid solution composed of N_1 molecules of type 1 and N_2 molecules of type 2, the total number of molecules $N_1 + N_2$ being designated by N . Following the general lines of Guggenheim's method (2), we span the volume v occupied by the solution by a virtual lattice, dividing it into N cells of equal size. Neglecting configurations in which two or more molecules occupy a single cell, we may express the partition function of the system as follows²

$$f = \sum_c e^{-\beta E(c)} Q(c)$$

$$\beta = 1/kT \quad (1)$$

where the sum extends over all configurations, c , of the system, the term "configuration" being employed in a special sense here to designate a specific distribution of the cells among the N molecules.³ $E(c)$ is the energy of the system in the given configuration when each molecule is situated at the origin of the cell which it occupies, and $Q(c)$ is a vibrational partition function appropriate to the given configuration, analogous to the lattice

² The formulation, equation 1, is really of value only for spherically symmetric molecules of equal size. However, if formally applied to non-spherical molecules, the factors, $Q(c)$, are understood to include rotational contributions to the partition function in the given configuration, and the free volume factors, v , in equation 2 should properly include a factor in rotational configuration space.

³ By considering the distribution of cells among molecules rather than molecules among cells, we avoid the necessity of dividing by $N_1! N_2!$, since we make no distinction between configurations differing only in the permutation of identical molecules.

vibrational partition function of a crystal. In the theory of Guggenheim $Q(c)$ is assumed independent of configuration and composition and is expressed in the following form

$$Q(c) = (2\pi m_1 kT)^{3N_1/2} (2\pi m_2 kT)^{3N_2/2} v^{N_1 + N_2} \quad (2)$$

where m_1 and m_2 are the masses of the two molecular types and v is the free volume of a molecule in any cell.⁴ On the basis of equation 2 and the assumption that the energy $E(c)$ is independent of configuration, Guggenheim deduces the laws of the regular solution of Hildebrand. We shall employ the first assumption, embodied in equation 2, but not the second. By taking account of the fluctuations in energy among the various configurations, we are able to investigate the ordering effect of a given molecule on its neighbors and the resulting deviations from the laws of the regular solution.

A configuration of the system may be uniquely specified by a set of numbers $\eta_1 \dots \eta_N$, stating the numbers of molecules of type 1 in each of the N cells. Each variable η_a may assume one of two values, zero or unity. Equally suitable for the purpose is the set $\rho_1 \dots \rho_N$, stating the number of molecules of type 2 in each cell. Obviously these sets are not independent, but for each cell a the relation, $\eta_a + \rho_a = 1$, holds. Nevertheless, for the sake of symmetry in notation, we shall find it convenient to employ both sets of variables. The following sum relations, satisfied by the η 's and the ρ 's, are important.

$$\sum_{a=1}^N \eta_a = N_1; \quad \sum_{a=1}^N \rho_a = N_2 \quad (3)$$

where the sums extend over all cells.

In calculating the energy, $E(c)$, of a given configuration, we shall neglect the interaction of each molecule with all but its z nearest neighbors, an approximation which is fairly good, since we are concerned with non-polar molecules coupled by short-range intermolecular forces. If there is no volume change on mixing the pure liquid constituents 1 and 2, the energy then has the form

$$E = E_0 + NV_0 p$$

$$V_0 = z[V_{12} - \frac{1}{2}(V_{11} + V_{22})] \quad (4)$$

where E_0 is the energy, $E_1 + E_2$, of the two pure liquids before mixing, V_{11} , V_{22} , and V_{12} are the mutual energies of the indicated types of nearest

⁴ The free volume v differs from that of Eyring and Hirschfelder, since the latter authors give equal weight to configurations in which two or more molecules are in a single cell. (See Rice: J. Chem. Phys. 6, 476 (1938).) The distinction is of no practical importance in the present discussion, since the free volume does not appear in the free energy of mixing.

neighbor pair, and p is a variable depending upon configuration in the following manner

$$p = (1/Nz) \sum_{a,b=1}^N \lambda_{ab} \eta_a \rho_b \quad (5)$$

where λ_{ab} is unity if the cells a and b are neighbors, and zero otherwise. Evidently we may write

$$\sum_{b=1}^N \lambda_{ab} = z \quad (6)$$

for any cell a .

The Gibbs free energy of mixing, ΔF , equal to ΔA , the work content change, if there is no volume change on mixing (8), is related to the partition functions of the solution and the pure liquids before mixing, f , f_1 , and f_2 , respectively, in the following manner

$$\begin{aligned} e^{-\beta \Delta F} &= f/(f_1 f_2) \\ f_1 &= (2\pi m_1 kT)^{3N_1/2} v^{N_1} \\ f_2 &= (2\pi m_2 kT)^{3N_2/2} v^{N_2} \end{aligned} \quad (7)$$

and f is given by equations 1 and 2. Equations 1, 2, 4, and 7 then allow us to write

$$\begin{aligned} e^{-\beta \Delta F} &= \sum_p \omega(p) e^{-N\alpha p} \\ \alpha &= V_0/kT \end{aligned} \quad (8)$$

where the sum extends over all values of p consistent with condition 3, and $\omega(p)$ is the number of configurations corresponding to a given value of p . Evidently we have

$$\sum_p \omega(p) = \binom{N}{N_1} \quad (9)$$

where the binomial coefficient $\binom{N}{N_1}$ is the total number of configurations of the system, equal to the number of ways in which the N cells may be distributed among N_1 molecules of type 1 and N_2 molecules of type 2. We define a distribution function, $\varphi(p)$, normalized to unity by the relation

$$\omega(p) = \binom{N}{N_1} \varphi(p) \quad (10)$$

The free energy of mixing, ΔF , may then be written

$$\begin{aligned}\Delta F/kT &= N_1 \log x_1 + N_2 \log x_2 - \log \sigma \\ \sigma &= \sum_p \varphi(p) e^{-N\alpha p}\end{aligned}\quad (11)$$

where the factorials of large numbers in $\binom{N}{N_1}$ have been evaluated by Stirling's formula and x_1 and x_2 are the mole fractions N_1/N and N_2/N of the two components.

The extreme difficulty of determining the distribution function, $\varphi(p)$, prevents the direct evaluation of the sum σ . However, its logarithm may be expanded in a power series in α , the coefficients of which involve the moments of $\varphi(p)$.

$$\log \sigma = \sum_{n=1}^{\infty} \frac{\lambda_n}{n!} (-N\alpha)^n \quad (12)$$

where the quantities, λ_n , are the semi-invariants of Thiele,⁶ which are related to the moments M_n of $\varphi(p)$ by the following set of linear equations

$$\begin{aligned}\sum_{m=1}^n \binom{n-1}{m-1} \lambda_m M_{n-m} &= M_n; \quad n = 1, 2, \dots \\ M_n &= \sum_p p^n \varphi(p)\end{aligned}\quad (13)$$

Solution of equations 13 yields for the first few semi-invariants

$$\begin{aligned}\lambda_1 &= M_1 \\ \lambda_2 &= M_2 - M_1^2 \\ \lambda_3 &= M_3 - 3M_1M_2 + 2M_1^3\end{aligned}\quad (14)$$

For the calculations of the moments, M_n (equation 13), it is convenient to introduce the variables $\eta_1 \dots \eta_N$ as indices of summation, since p depends upon these variables (equation 5). From the definitions of $\varphi(p)$ and $\omega(p)$ we may write

$$M_n = \binom{N}{N_1}^{-1} \sum_{\substack{\eta_1 \dots \eta_N=0 \\ \sum_{a=1}^N \eta_a = N_1}}^1 [p(\eta_1, \dots, \eta_N)]^n \quad (15)$$

We note that if m is a positive exponent

$$\eta_a^m = \eta_a; \quad \rho_a^m = \rho_a \quad (16)$$

⁶ See A. Fisher: *Mathematical Theory of Probabilities*, 2nd edition. The Macmillan Co., New York (1926).

since η_a and ρ_a are restricted to the values zero and unity. This fact, together with equation 5, leads to the following expression for the moments,

$$M_n = (1/Nz)^n \sum_{r=1}^n \sum_{s=1}^n \nu_{rs}^{(n)} y_{rs}$$

$$y_{rs} = \left(\frac{N}{N_1} \right)^{-1} \sum_{\substack{\eta_1 \dots \eta_N = 0 \\ \sum_{a=1}^N \eta_a = N_1}}^1 \eta_{a_1} \dots \eta_{a_r} \rho_{b_1} \dots \rho_{b_s} \quad (17)$$

where $\nu_{rs}^{(n)}$ is the number of terms in

$$\left(\sum_{a,b=1}^N \lambda_{ab} \eta_a \rho_b \right)^n$$

involving $r + s$ distinct indices (cells) $a_1, \dots, a_r, b_1, \dots, b_s$. The validity of equation 17 of course assumes that y_{rs} is independent of the particular set of $r + s$ cells involved. This we shall show to be the case. The product, $\eta_{a_1} \dots \eta_{a_r} \rho_{b_1} \dots \rho_{b_s}$ is unity if r specified cells $a_1 \dots a_r$ are occupied by molecules of type 1 and s specified cells $b_1 \dots b_s$ are occupied by molecules of type 2. Otherwise it is zero, since it vanishes if any of the $r + s$ factors is zero. Thus the sum on the right-hand side of equation 17 is exactly equal to the number of ways in which $N - r - s$ specified cells may be distributed among $N_1 - r$ molecules of type 1 and $N_2 - s$ molecules of type 2, equal to $\binom{N-r-s}{N_1-r}$, multiplied by the number of ways r specified cells may be distributed among r molecules of type 1 and s specified cells among s molecules of type 2, equal to unity. Thus we have the following expression for y_{rs} :

$$y_{rs} = \left(\frac{N}{N_1} \right)^{-1} \binom{N-r-s}{N_1-r} \quad (18)$$

a result which is independent of the particular set of $r + s$ specified cells involved. We shall not attempt to give a general expression for the coefficients $\nu_{rs}^{(n)}$, merely calculating them for certain specific values of n . The first moment, M_1 , is easily calculated, $\nu_{11}^{(1)}$ being equal to Nz , the total number of terms in the sum (equation 5). Thus we have by equations 17 and 18,

$$M_1 = \left(\frac{N}{N_1} \right)^{-1} \binom{N-2}{N_1-1} = x_1 x_2 \left(1 + \frac{1}{N} \right) + O(1/N^2) \quad (19)$$

where $O(1/N^2)$ denotes terms bearing a ratio or order $1/N^2$ to the initial term. For the calculation of the second moment M_2 , we find by inspection of the second power of the sum in equation 5

$$\begin{aligned}\nu_{11}^{(2)} &= Nz \\ \nu_{12}^{(2)} &= \nu_{21}^{(2)} = Nz(z-1) \\ \nu_{22}^{(2)} &= N^2 z^2 - 4Nz^2 + 2Nz\end{aligned}\quad (20)$$

We note that the sum of the $\nu_{rs}^{(n)}$ is less than the total number of terms, $(Nz)^n$, in the sum,

$$\left(\sum_{a,b=1}^N \lambda_{ab} \eta_a \rho_b \right)^n$$

since any term in which an index a is equal to an index b vanishes by virtue of the relation $\eta_a + \rho_a = 1$, requiring $\eta_a \rho_a$ always to vanish. By equations 17, 18, and 20 we obtain, after some algebraic reductions,

$$M_2 = x_1^2 x_2^2 \left(1 + \frac{2(z+1)}{Nz} \right) + O(1/N^2) \quad (21)$$

The moment M_3 may be calculated by a similar procedure. Finally we obtain with the aid of equation 14 the following expressions for the semi-invariants.

$$\begin{aligned}\lambda_1 &= x_1 x_2 \\ \lambda_2 &= 2x_1^2 x_2^2 / Nz \\ \lambda_3 &= -4x_1^2 x_2^2 (x_1 - x_2)^2 / N^2 z^2\end{aligned}\quad (22)$$

In the calculation of λ_3 , the details of which have not been given, it is necessary to retain terms of order N^{-2} in M_1 and M_2 . The method just described for the calculation of the moments is similar in principle to that employed by Van Vleck in his treatment of the Heisenberg theory of ferromagnetism. An alternative method has been described by the writer in an earlier article which involves the use of interpenetrating lattices. It may equally well be used in the present calculations.

Equations 11, 12, and 22 lead to the following expression for the free energy of mixing of the solution:

$$\begin{aligned}\Delta F/NkT &= x_1 \log x_1 + x_2 \log x_2 + \alpha x_1 x_2 - (\alpha^2/z) x_1^2 x_2^2 \\ &\quad - (2\alpha^3/3z^2) x_1^2 x_2^2 (x_1 - x_2)^2\end{aligned}\quad (23)$$

Equation 23 is valid to terms in the fourth and higher powers of α . By means of the thermodynamic formulas,

$$E = \partial(F/T)/\partial(1/T)$$

and

$$S = - \partial F / \partial T$$

expressions for the average energy and entropy of mixing may be obtained.

$$\begin{aligned} \Delta E / NkT &= \alpha x_1 x_2 - (2\alpha^2/z)x_1^2 x_2^2 - (2\alpha^3/z^2)x_1^2 x_2^2 (x_1 - x_2)^2 \\ \Delta S / Nk &= -x_1 \log x_1 - x_2 \log x_2 - (\alpha^2/z)x_1^2 x_2^2 - (4\alpha^3/3z^2)x_1^2 x_2^2 (x_1 - x_2)^2 \end{aligned} \quad (24)$$

The chemical potentials of the two components may be obtained by differentiation of ΔF with respect to N_1 and N_2 , respectively, at constant temperature, pressure, and number of moles of the other component.

$$\left. \begin{aligned} (\mu_1 - \mu_1^0) / RT &= \log x_1 + \alpha x_2^2 - (\alpha^2/z)x_1 x_2^2 (3x_2 - 1) + \dots \\ (\mu_2 - \mu_2^0) / RT &= \log x_2 + \alpha x_1^2 - (\alpha^2/z)x_1^2 x_2 (3x_1 - 1) + \dots \end{aligned} \right\} \quad (25)$$

where μ_1^0 and μ_2^0 are the chemical potentials of the pure liquid components. The retention of terms in the first power of α alone in equations 23, 24, and 25 leads to the laws of the regular solution. The terms in the higher powers of α represent the ordering effect of each molecule on its neighbors and the resulting deviation from random distribution.

The constant V_0 , equal to αkT , may be computed from the heat of solution at any temperature by means of equation 24. Since there is no volume change on mixing, ΔE is equal to ΔH , the negative of the integral heat of solution. If we designate by L the negative of the integral heat of solution per mole of an equimolal mixture of the components and retain only terms in α^2 in equation 24, we obtain

$$\alpha = z [1 - (1 - 8L/zRT)^{1/2}] \quad (26)$$

In the greater number of non-polar liquid mixtures L is positive, corresponding to a negative heat of solution, and α and V_0 are also positive.

When α is positive there exists a critical solution temperature below which the solution separates into two phases. Although in most non-polar liquid mixtures this temperature lies so low that the solution is unstable with respect to solid phases before it is reached, a discussion of the question is not without theoretical interest. For the coexistence of two liquid phases γ and ϵ , the conditions of heterogeneous equilibrium require

$$\begin{aligned} \mu_1^{(\gamma)} &= \mu_1^{(\epsilon)} \\ \mu_2^{(\gamma)} &= \mu_2^{(\epsilon)} \end{aligned} \quad (27)$$

where $\mu_1^{(\gamma)}$, $\mu_2^{(\epsilon)}$, etc., are the chemical potentials of the components in the respective phases. From the symmetry of equations 25 remark that in either phase

$$\begin{aligned}\mu_1^{(\gamma)} - \mu_1^0 &= \mu(x_1^{(\gamma)}) \\ \mu_2^{(\gamma)} - \mu_2^0 &= \mu(x_2^{(\gamma)})\end{aligned}\quad (28)$$

$$\mu(x)/RT = \log x + \alpha(1-x)^2 - (\alpha^2/z)x(1-x)^2(2-3x)$$

Thus equations 27 reduce to

$$\begin{aligned}\mu(x_1^{(\gamma)}) &= \mu(x_1^{(\epsilon)}) \\ \mu(x_2^{(\gamma)}) &= \mu(x_2^{(\epsilon)}) \\ x_1^{(\gamma)} + x_2^{(\gamma)} &= 1 \\ x_1^{(\epsilon)} + x_2^{(\epsilon)} &= 1\end{aligned}\quad (29)$$

Equations 29 are satisfied if

$$\begin{aligned}\mu\left(\frac{1+\delta}{2}\right) &= \mu\left(\frac{1-\delta}{2}\right) \\ x_1^{(\gamma)} &= x_2^{(\epsilon)} \\ x_2^{(\gamma)} &= x_1^{(\epsilon)} \\ x_1^{(\gamma)} + x_2^{(\gamma)} &= 1\end{aligned}\quad (30)$$

where δ is the difference, $x_1^{(\gamma)} - x_1^{(\epsilon)}$ or $x_2^{(\epsilon)} - x_2^{(\gamma)}$, in composition of the two phases. Equations 28 and 30 lead to the following condition on δ :

$$\begin{aligned}\delta &= \tan h(B\delta) \\ B &= \frac{1}{2} [\alpha - (\alpha^2/z)(1 - \delta^2)]\end{aligned}\quad (31)$$

For two phases to coexist, equation 31 must have a real solution differing from zero, the vanishing solution corresponding to the trivial case in which the phases are identical. A non-vanishing real solution exists only if B is greater than unity. Thus there exists a critical value α_c which must be exceeded for two phases to coexist, satisfying the equation

$$\begin{aligned}\alpha_c^2 - 2z\alpha_c + 4z &= 0 \\ \alpha_c &= z[1 - (1 - 4/z)^{1/2}]\end{aligned}\quad (32)$$

and a critical solution temperature, T_c , below which two phases can coexist.

$$T_c = V_0/k\alpha_c \quad (33)$$

For a regular solution in which only the linear term in α is retained, T_c is equal to $0.5 V_0/k$. However, from equation 32 we calculate for α_c a value, 2.34, with body-centered packing, $z = 8$, and a critical solution temperature $0.427 V_0/k$. This is lower than the regular solution value by 15 per cent. Thus the local order established by a molecule among its

neighbors opposes the tendency of the solution to separate into two phases. The latter process may be regarded as a macroscopic mechanism for establishing order, satisfying the tendency of a molecule to make its environment rich in its own species when α is positive. This tendency may be partially satisfied without separation into two phases through the microscopic ordering mechanism by means of which a molecule establishes a local composition richer in its own species than the solution in bulk.

A remark about the relative magnitudes of the various terms in the free energy of mixing, equation 23, is perhaps appropriate. We shall consider only the regular solution term $\alpha x_1 x_2$ and the quadratic term $(\alpha^2/z)x_1^2 x_2^2$. The latter term bears a ratio of $\alpha x_1 x_2/z$ to the regular solution term. With z equal to eight in an equimolar mixture at the critical solution temperature, this ratio is equal to 0.07. Thus the local order effect produces a rather small deviation from the regular solution, smaller, indeed, than one might surmise on qualitative grounds.

Rushbrooke (6) obtains an expression for the free energy of mixing in which the local order contribution involves an exponential. When the exponential is expanded and notations are brought into correspondence, his equation and equation 23 are in agreement in the linear and quadratic terms in α . However, the cubic terms in α do not agree, and indeed Rushbrooke's term depends upon composition in an entirely different manner from our own. Since the present treatment provides an exact method for the expansion of the free energy in powers of α , within the frame of the simplifying assumptions underlying both theories, it would appear that not much significance can be attached to the higher powers of α or $1/T$ in the expansion of Rushbrooke's exponential. The conclusions based upon the two treatments are, however, essentially the same.

When we come to consider the influence of the local order effect on the deviation of actual solutions from regular behavior, we find that it is generally overshadowed by other effects. An analysis of the data on a large number of non-polar liquid mixtures by Professor Scatchard (9) shows that in solutions for which ΔE and α are positive, the entropy of mixing, in excess of the ideal value, $R[-x_1 \log x_1 - x_2 \log x_2]$, is in general positive, whereas the local order contribution, $-(\alpha^2/z)x_1^2 x_2^2$, from equation 24 is always negative. We shall not speculate on the nature of the other effects at the present. However, they are doubtless concealed in the vibrational factors $Q(c)$ of the partition function (equation 1). Moreover it seems certain that the Guggenheim approximation, in which these factors are treated as independent of both composition and configuration, is far too drastic to provide an exact theory.

In conclusion, we remark that although the local order effect is relatively small and generally overshadowed by other influences, an analysis of the type which has been described seems not without value, since these conclusions could scarcely have been reached by qualitative reasoning.

REFERENCES

- (1) BETHE, H.: Proc. Roy. Soc. (London) **A150**, 552 (1935).
- (2) GUGGENHEIM, E. A.: Proc. Roy. Soc. (London) **A148**, 304 (1935).
- (3) HILDEBRAND, J. H.: Solubility, American Chemical Society Monograph, 2nd edition. The Chemical Catalog Co., Inc., New York (1936).
- (4) HILDEBRAND, J. H., AND WOOD, S. E.: J. Chem. Phys. **1**, 817 (1933).
- (5) KIRKWOOD, J. G.: J. Chem. Phys. **6**, 70 (1938).
- (6) RUSHBROOKE: Proc. Roy. Soc. (London) **A166**, 296 (1938).
- (7) SCATCHARD, G.: Chem. Rev. **8**, 321 (1931).
- (8) SCATCHARD, G.: Trans. Faraday Soc. **33**, 160 (1937).
- (9) SCATCHARD, G., AND HAMER, W. J.: J. Am. Chem. Soc. **57**, 1805 (1935).

SEVERAL SOLUTIONS OF NON-POLAR SUBSTANCES¹

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I. THE SYSTEM IODINE-CARBON TETRACHLORIDE THROUGH A RANGE OF 161°C.

The large deviations from Raoult's law shown by solutions of iodine with carbon tetrachloride, and their dependence upon differences in internal pressure rather than upon changes in molecular species, have made this system one of the most interesting examples of a non-ideal solution, and it has been dealt with in several previous papers (6, 7). In the most recent of these the course of the solubility curve for the range 0° to 50°C. was made the basis for predicting the existence of two liquid phases above the melting point of iodine. This proved to be true, with a consolute temperature of 161°C., well within the limit of accuracy of the prediction.

It has seemed desirable to determine a few points within the long interval between 50° and 130°C., so as to have a better record of the temperature dependence. As part of this program, direct determinations of the heat of fusion of iodine and the heat capacities of both solid and liquid have been carried out in this laboratory by K. J. Frederick (3). This has lent more confidence to our calculations of the ideal solubility of the solid iodine.

Iodine from Kahlbaum and carbon tetrachloride from the Eastman Kodak Company were used without further purification than drying the latter with calcium chloride. The proper amounts were put into a simple Pyrex glass apparatus consisting of a horizontal, cylindrical mixing compartment, with two side bulbs attached to the vertical stem. The charge in the main compartment was frozen in liquid air, and the apparatus was evacuated and sealed. The apparatus was placed in a thermostat and rocked so that the liquid surged vigorously back and forth. When it was judged that equilibrium had been reached, the apparatus was tilted so as to pour solution into one of the side bulbs. The great density of iodine, together with the fact that the excess solid mats together, made it unlikely that any solid particles would be carried over. The apparatus was then cooled, and the bulb was sealed off and weighed. The bulb was opened

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and its iodine content determined by titration with thiosulfate. The glass was weighed and the carbon tetrachloride was determined by difference. Table 1 gives the results of four determinations. These correlated so well with each other and with the data for the same system at high and at low temperatures that they are sufficiently accurate for our purpose.

Table 2 shows the correlation of all the data for this system, including the solubility of solid iodine from 0° to 100°C. and of liquid iodine from

TABLE 1
Solubility of iodine in carbon tetrachloride

TEMPERATURE	IODINE	IODINE
°C.	weight per cent	mole per cent
80.2	11.53	7.35
97.0	20.55	13.56
99.5	22.00	14.59
99.9	22.16	14.71

TABLE 2
Correlation of data for the system iodine-carbon tetrachloride

<i>t</i>	$-\log N_1'$	$\log N_2'$	v_1	v_2	\mathcal{V}_1	\mathcal{V}_1'	$-\log N_2$	<i>D</i>
°C.								
0	0.790		94.4	58.5	0.998		2.379	5.82
25	0.582		97.5	59.6	0.993		1.940	5.61
35	0.503		98.8	60.1	0.990		1.798	5.60
50	0.394		100.7	60.8	0.984		1.556	5.40
80.2	0.193		104.8	62.2	0.954		1.134	5.18
97.0	0.093		107.0	65.4	0.912		0.868	4.91
99.5	0.078		107.5	65.5	0.906		0.836	4.90
99.9	0.075		107.5	65.5	0.905		0.833	4.88
150		0.086	116	66.0	0.686	0.282	0.347	4.43
154		0.099	117	66.2	0.648	0.316	0.306	4.38
158		0.119	118	66.4	0.594	0.361	0.260	4.18
161		0.167	118.5	66.5	0.462	0.462	0.167	4.28

150° to 161°C. This is done by calculating the parameter *D* in the equation (7)

$$RT \ln (a_2/N_2) = v_2 \mathcal{V}_1^2 D^2$$

This becomes

$$RT \ln (N_2'/N_2) = v_2 (\mathcal{V}_1'^2 - \mathcal{V}_1'^2) D^2$$

for two liquid phases below the critical solution temperature and

$$1.985 T_c (N_1 v_1 + N_2 v_2)^3 = 2 v_1^2 v_2^2 N_1 N_2 D^2$$

at that point. Here n is mole fraction, a is activity referred to the pure liquid as standard, v is molal volume, \mathcal{V} is volume fraction, i.e.,

$$\mathcal{V}_1 = N_1 v_1 / (N_1 v_1 + N_2 v_2)$$

Subscripts refer to the components, and N_2 and N_2' in the second equation refer to the mole fractions of iodine in the two liquid phases in equilibrium. The value of a_2 for the solid iodine is calculated by aid of the equation:

$$R \ln a_2 = R \ln N_2' = - \int_T^{T_m} (\mathcal{H}^0 - \mathcal{H}^*) d(1/T)$$

where \mathcal{H}^* is the heat content of the pure solid and \mathcal{H}^0 that of the liquid, T_m is the melting point, and N_2' the ideal solubility. $\mathcal{H}^0 - \mathcal{H}^*$ is the heat of fusion at the melting point, but this varies with temperature depending

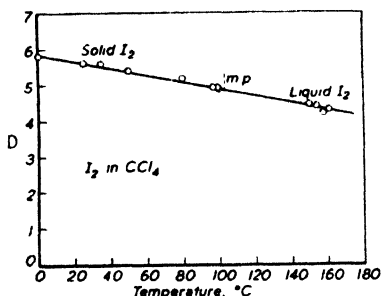


FIG. 1. Plot of D against temperature for iodine in carbon tetrachloride

on the difference in heat capacity of the solid and liquid forms. The data previously referred to have been used for the present purpose. However, in view of the peculiar form found for the dependence of the heat content of solid iodine with temperature, it was thought preferable to plot the data for \mathcal{H}^0 and \mathcal{H}^* against $1/T$, assume that \mathcal{H}^0 varies linearly with T below the melting point as it seems to do above, and integrate graphically between $1/T_m$ and $1/T$. This process yielded the values of $-\log N_2'$ given in table 2. In the portion of the table referring to liquid iodine, $\log N_2'$ is replaced by $\log N_2$, referring to the second liquid phase.

The last column gives the values of D calculated from all the data, and these are plotted against temperature in figure 1. That the points show so little variation from the smooth line through them is evidence of the very satisfactory correlation of the data, all the more remarkable in that it includes a range of 161°C. and both solid-liquid and liquid-liquid systems; that the line is straight is indeed surprising, since the effect of clustering near the critical point is ignored in the derivation of the equation.

II. OSMIUM TETROXIDE SOLUTIONS WITH CARBON TETRACHLORIDE

An interesting paper has recently been published by Anderson and Yost (1), giving properties of osmium tetroxide in carbon tetrachloride solutions. They show that the distribution ratio of the tetroxide between carbon tetrachloride and water varies with the concentration, and that the vapor pressure of carbon tetrachloride from its solutions with the tetroxide does not follow Raoult's law but agrees rather well with the assumption of an equilibrium between OsO_4 and $(\text{OsO}_4)_4$. These authors mention the other possible explanation of the fact that this solution is not ideal, i.e., that the molecular field strengths or internal pressures of these two substances are sufficiently different to cause departure from Raoult's law without the presence of any definite polymer of either species. Polymerization in solution is contraindicated by the evidence that even in the pure liquid state osmium tetroxide behaves as a normal liquid.

The vapor pressure has been measured by Ruff and Tschirch (12), by von Wartenberg (16), and by Ogawa (11). Plotted in the usual way, log

TABLE 3
Data for the system osmium tetroxide-carbon tetrachloride

x_2	p_1	a_1	a_1/x_1	γ_2	D
0.395	7.86	0.686	1.133	0.278	3.13
0.599	6.19	0.540	1.344	0.471	2.84
0.693	5.39	0.470	1.530	0.574	2.81
Mean					2.93

p against $1/T$, the values agree rather well, those of Ogawa appearing most consistent, and give a molal heat of vaporization of about 9040 cal. at the boiling point ($130^\circ\text{C}.$), corresponding to a Trouton quotient of 22.4. This test and the more rigid test by the aid of the "Hildebrand rule" (9) indicate a normal liquid. This conclusion is further confirmed by surface tension measurements by Ogawa.

I shall next show that the extent of the departure of the solutions of the tetroxide in carbon tetrachloride from Raoult's law is approximately what could have been predicted from the difference in their internal pressures as measured by the energy of vaporization per cubic centimeter, $\Delta E/v$. Actually we use the square root of this quotient. For carbon tetrachloride at $25^\circ\text{C}.$ this is 8.54 (cal. per cubic centimeter)¹. The vapor pressures of the osmium tetroxide just cited give $\Delta H = 9800$, extrapolated to $25^\circ\text{C}.$, and $\Delta E = 9200$ at the same temperature. The liquid densities observed by Ogawa give a molal volume of 58.0 cc. extrapolated to $25^\circ\text{C}.$ from the melting point ($40^\circ\text{C}.$), hence $(\Delta E/v)^{\frac{1}{2}} = 12.60$. Let us now obtain a value by using the vapor pressure data of Anderson and Yost for the solution

in connection with the approximation formula, equation 1. We designate a_1 as the activity of carbon tetrachloride, which we may set equal to its partial vapor pressure, p_1 , divided by its saturation pressure, 11.46 cm. at 25°C.; N_1 as its mole fraction in solution; v_1 as its molal volume at 25°C., 97.1 cc.; and \mathcal{V}_2 as the volume fraction of the osmium tetroxide in solution.

Table 3 gives the values for those solutions sufficiently concentrated in the tetroxide to show deviations from Raoult's law. If we add the mean value of D to the value of $(\Delta E/v)^{\frac{1}{2}}$ for carbon tetrachloride, 8.54, we obtain 11.5, which we may compare with the value 12.6 for osmium tetroxide obtained above from its energy of vaporization. The agreement is sufficiently good, in view of the extrapolations and approximations involved, to indicate the adequacy of this explanation for the departure of these solutions from Raoult's law.

III. SOLUTIONS OF HEXANE WITH HEXADÉCANE²

Guggenheim (5), at the Symposium on Intermolecular Forces held by the Faraday Society in 1936, raised the interesting question of the validity of Raoult's law for solutions of components of equal molecular field strength but unequal volumes. In a subsequent publication (8) I discussed this problem with particular reference to solutions of normal paraffins, in which a parallel arrangement of molecules might be assumed, and reached the conclusion that the number of different configurations possible in such solutions corresponded to an entropy of transfer of component 2 from pure liquid to solution of $-R \ln N_2$. This is the same as for a solution of molecules of the same size, in which case, as in a solid solution with a fixed crystal lattice, the entropy is that of an ideal solution. More recently Fowler and Rushbrooke (2) have made a searching application of statistical theory to the case of two components, the molecules of one of which occupy one point each in a lattice, while the molecules of the other occupy two with all possible orientations permitted. The result was "that mere change of size is sufficient to cause deviations from linearity; . . . though definite, the deviation is unexpectedly small for so large a change of size." Several factors involved, however, could not be estimated with any precision, so that the authors did not claim that the deviation had been established with certainty.

In my paper (8) I was able to cite only very limited experimental evidence, consisting of data on solutions of diphenyl and benzene, butane and heptane, and dicetyl in propane, butane, and heptane. In the case

² I wish to acknowledge my indebtedness to Mr. John M. Sweny for assistance in this investigation. We hope to present later more numerous and more precise results, in order to detect any deviations of the type deduced by Fowler and Rushbrooke.

of dicetyl, the uncertainty regarding the ideal solubility limited the argument to the equality of solubility in butane and heptane and the inference that this is the ideal solubility. This equality has since been extended by Sayer (13) to several other normal paraffin solvents,—hexane, octane, decane, and dodecane.

It has seemed worth while to seek a direct experimental check of this interesting matter. For this a system likely to conform as closely as possible to the model of parallel arranged molecules assumed in my previous paper was desired. This indicated the choice of one component with a melting point not far below the temperature of the experiment. Normal hexadecane, melting at 16°C., may be assumed to retain in the liquid at 25°C. much of the parallel arrangement of molecules which it undoubtedly possesses in the solid form. For the other component hexane was selected, which has a vapor pressure of 149 mm. at 25°C., a convenient magnitude to measure by simple means. The vapor pressure of hexadecane at 25°C.

TABLE 4
Activity of hexane in solutions with hexadecane at 25°C.

MOLE FRACTION N_1	VAPOR PRESSURE p_1	ACTIVITY $a_1 = p_1/p_1^0$	ACTIVITY COEFFICIENT a_1/N_1
1.000	149.7	1.000	
0.708	106.2	0.709	1.001
0.648	99.6	0.665	1.025
0.626	92.7	0.619	0.989
Mean			1.005

is negligible. A small stock of each component in very pure form was available, hence it was necessary to use an appropriate method. The method used years ago in investigating the vapor pressure of amalgams (10) was selected. The solution was confined in a U-tube sealed at one end; the other end was connected to a hydrogen-filled system provided with a manometer whose pressure could be varied to balance the vapor pressure in the closed limb. Escape of hexane vapor up the long limb was prevented by a condenser cooled by solid carbon dioxide.

Partial results are reported here on account of their pertinence to this symposium. Further and more precise results are to be sought.

Table 4 gives a brief summary of the measurements thus far obtained. Each pressure recorded represents the mean of a number of observations. The activity coefficients in the last column differ from unity only by an amount within the experimental error, indicating that this system obeys Raoult's law rather closely, in spite of the fact that the length of the molecule of the one component is 2.7 times that of the other.

IV. TELLURIUM TETRACHLORIDE AND IODINE³

In the table of internal pressures of liquids at 25°C. given in the monograph on solubility (7), iodine and tellurium tetrachloride have identical values and, if no disturbing factors were present, should give ideal solutions with each other. This can not be tested directly, as neither substance can be supercooled in the liquid state to this temperature, and the data in the table are of use only for predicting their solubilities in substances which are liquid at ordinary temperatures. If we turn to temperatures above the melting point of iodine, where an experimental check is possible, we obtain values for their internal pressures which are still not far apart. Iodine melts at 113.4°C., and at 140°C. its molal heat of vaporization, calculated from the vapor pressure table in the International Critical Tables, is 10,620 cal. The molal volume of liquid iodine at this temperature is 65.2 cc., hence the energy of vaporization per cubic centimeter, $\Delta E/v$, is 156.4 cal. The corresponding values for tellurium tetrachloride, calculated from the data of Simons (14), are $\Delta H = 18,400$ cal.; $v = 100$ cc. (extrapolated); $\Delta E/v = 175.8$ cal. per cubic centimeter. The deviation from Raoult's law, in terms of the approximate equation frequently used for this purpose, is determined by the parameter,

$$D^2 = [(\Delta E_1/v_1)^{\frac{1}{2}} - (\Delta E_2/v_2)^{\frac{1}{2}}]^2$$

In this case $D^2 = 0.61$, which corresponds to only a moderate departure from ideality.

However, tellurium tetrachloride is a substance whose molecular field may be rather different in type as well as in strength from tetrachlorides of the elements from carbon to tin. Its melting and boiling points are 225° and 390°C., respectively, while the corresponding points for stannic chloride, for example, are -30° and 113°C. It has an electric conductivity in the liquid state at 236°C. of 0.115 mhos, according to Vogt and Biltz (15). The application of the "Hildebrand rule" (9) to the vapor pressure curve reveals an entropy of vaporization of 30.6 units at a concentration of vapor of 0.00507 mole per liter, at which normal liquids show an entropy of vaporization of only 27.4.

We have undertaken, accordingly, to learn whether or not tellurium chloride gives regular and approximately ideal solutions with iodine.

Knowing, as we now do, the heat of fusion and specific heats of tellurium tetrachloride from the measurements of Frederick and Hildebrand (4), it is possible to use the freezing point-composition diagram for our purpose. This was determined by means of cooling curves with solutions sealed in Pyrex tubes provided with central wells for the insertion of a calibrated

³ It is our intention to study this system more thoroughly. I am indebted to Mr. D. J. Turner for the measurements reported here.

copper—"advance" thermocouple. The iodine was of high purity and was resublimed once. The tellurium tetrachloride was redistilled.

Table 5 gives the points determined. They are plotted in figure 2 along with the ideal curves calculated from the heats of fusion. It is evident that the actual points are far from the ideal curves, indicating that the

TABLE 5
The system iodine-tellurium tetrachloride

TELLURIUM TETRACHLORIDE		SOLID PHASE
mole per cent	°C.	
0	113.4	I ₂
0.88	111.9	I ₂
(2.0)	110.0	Eutectic
2.82	111.8	TeCl ₄
3.81	113.0	TeCl ₄
6.62	117.0	TeCl ₄
13.98	125.5	TeCl ₄
21.78	129.0	TeCl ₄
32.83	134.0	TeCl ₄

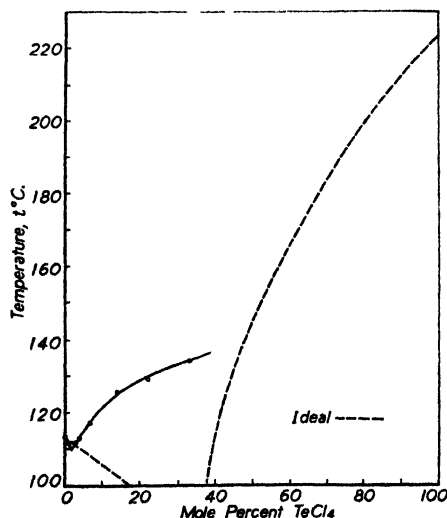


FIG. 2. Freezing point-composition diagram for iodine-tellurium tetrachloride

two components are actually very different. It is to be noted that the lowering of the freezing point of iodine is much greater than ideal, as it would be if the tellurium chloride were ionized, also that the flattening of the right-hand branch corresponds to an approach to immiscibility. This evidence is in line with the observation of Simons that tellurium tetrachloride has a negligible solubility in carbon tetrachloride at 100°C. Al-

though the low internal pressure of this solvent indicates only a small solvent power for this solute, if the solution is regular, this alone would not suffice to make it too small for observation.

SUMMARY

1. New determinations of the solubility of iodine in carbon tetrachloride in the region 80° to 100°C. bridge the gap heretofore existing between data for the solid from 0° to 50°C. and for the liquid from 150° to 161°C., the critical solution temperature. The trend with temperature of the parameter in the solubility equation which expresses the deviation from ideal behavior is quite uniform and shows no effect ascribable to clustering near the critical solution temperature.

2. Data for the vapor pressure of carbon tetrachloride in solution with osmium tetroxide are analyzed. It is shown that the deviation from Raoult's law is approximately of the amount predictable from the internal pressure difference of the components.

3. Preliminary figures for the vapor pressure of *n*-hexane from solutions with *n*-hexadecane indicate that, as predicted by theory, these solutions obey Raoult's law within the limit of error, in spite of the ratio of 2.7 for the lengths of the two species of molecule.

4. Freezing point data for the system iodine-tellurium tetrachloride show that, in spite of approximately equal internal pressures in the liquid state, these solutions are far from ideal, owing, probably, to a more or less salt-like character of the tellurium tetrachloride, giving a molecular field different in kind from that of iodine.

REFERENCES

- (1) ANDERSON, LEROY H., AND YOST, DON M.: J. Am. Chem. Soc. **60**, 1822 (1938).
- (2) FOWLER, R. A., AND RUSHBROOKE, G. S.: Trans. Faraday Soc. **33**, 1272 (1937).
- (3) FREDERICK, K. J., AND HILDEBRAND, J. H.: J. Am. Chem. Soc. **60**, 1436 (1938).
- (4) FREDERICK, K. J., AND HILDEBRAND, J. H.: J. Am. Chem. Soc. **60**, 2522 (1938).
- (5) GUGGENHEIM, E. A.: Trans. Faraday Soc. **33**, 151 (1937).
- (6) (a) HILDEBRAND, J. H., AND JENKS, C. W.: J. Am. Chem. Soc. **42**, 2180 (1920).
(b) NEGISHI, G. R., DONALLY, L. H., AND HILDEBRAND, J. H.: J. Am. Chem. Soc. **55**, 4793 (1933).
- (c) HILDEBRAND, J. H.: J. Am. Chem. Soc. **57**, 866 (1935).
- (d) HILDEBRAND, J. H.: J. Am. Chem. Soc. **59**, 2083 (1937).
- (7) HILDEBRAND, J. H.: Solubility of Non-electrolytes. Reinhold Publishing Corporation, New York (1936).
- (8) HILDEBRAND, J. H.: J. Am. Chem. Soc. **59**, 794 (1937).
- (9) HILDEBRAND, J. H.: J. Am. Chem. Soc. **37**, 970 (1915).
- (10) HILDEBRAND, J. H.: Trans. Am. Electrochem. Soc. **22**, 319 (1912).
- (11) OGAWA, E.: Bull. Chem. Soc. Japan **6**, 302 (1931).
- (12) RUFF, O., AND TSCHIRCH, F. W.: Ber. **46**, 929 (1913).
- (13) SAYER, W. F.: J. Am. Chem. Soc. **60**, 827 (1938).
- (14) SIMONS, J. H.: J. Am. Chem. Soc. **52**, 3488 (1930).
- (15) VOGT, A., AND BILTZ, W.: Z. anorg. allgem. Chem. **133**, 277 (1924).
- (16) VON WARTENBERG, H.: Ann. **440**, 97 (1924).

VAPOR-LIQUID EQUILIBRIUM. III^{1,2}

BENZENE-CYCLOHEXANE MIXTURES

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When our simple theory of liquid solutions was first proposed (13, 4) there was difficulty in finding experimental measurements of sufficient accuracy to test the theory. The amplification of the theory published later (14) put an even more severe demand on the experimental measurements. For only two mixtures of non-polar organic liquids could we determine the excess entropy of mixing at constant total volume, and in neither case could we be sure that the value found differed from zero by more than the experimental error.

As a first step in supplying accurate experimental results we have measured the vapor-liquid equilibrium of benzene-cyclohexane mixtures from 30° to 70°C. and the volumes of the liquid mixtures at 30°C. The measurements are sufficiently precise so that we have confidently expressed them analytically. The complete interpretation of this system would require measurements of the volumes through a range of temperatures and pressures, and confirmation of our results by measurements of heats of mixing and heat capacities would be desirable. However, our results show conclusively that this system is very far from regular, and that the excess entropy of mixing at constant total volume is about half as great as that at constant pressure. The change of the various thermodynamic functions with composition is also more complicated than our simple theory predicts, and the effect is slightly larger than predicted. A possible explanation of the excess entropy is discussed, which may also explain the other deviations.

The components were purified by rectification in a still with a column, 2.5 meters high and 19 mm. in internal diameter, made of Pyrex glass and packed with single turn Pyrex helices. The column is jacketed by two

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other glass tubes concentric with it and leaving air gaps about 5 mm. thick. The inner jacket is heated so that its top third has the same temperature as the top of the column, the bottom third has the same temperature as the bottom of the column, and the middle third has a temperature about halfway between those of the top and the bottom. The still is arranged so that all the vapors are condensed, and the condensate, before returning to the column, passes through a trap whose capacity may be varied from 50 cc. to 1200 cc.; the quantity of liquid in the pot may be varied from 75 cc. to 1500 cc. When the liquids are nearly pure, as in the present case, low-boiling impurities are removed by operating for a day with about 50 cc. in the trap, then the contents of the trap are discarded, and the operation is repeated the next day with another 50 cc. High-boiling impurities are removed by operating with most of the liquid in the trap and only about 75 cc. in the pot; at the end of each day the contents of the pot and the "hold-up" in the column are discarded together. Although we have not made a quantitative comparison, we believe that this method is more economical of material for the removal of low-boiling impurities than the usual distillation method, and that it has the great advantage of being as efficient for the removal of high-boiling impurities as for low.

A commercial synthetic "thiophene-free" benzene was rectified without preliminary purification. Three top fractions and three bottom fractions were discarded. The freezing point was taken in the presence of solid calcium chloride, as the simplest means of preventing errors from the very high humidity. The freezing point of $5.53^{\circ}\text{C}.$ did not decrease more than $0.005^{\circ}\text{C}.$ as half of the benzene was frozen. Our vapor pressure curve gives $80.10^{\circ}\text{C}.$ as the normal boiling point of our product. Timmermans and Martin (20) give $5.50^{\circ}\text{C}.$ and $80.20^{\circ}\text{C}.$, respectively, as the freezing and boiling points of benzene, and Smith and Matheson (18) give $80.094^{\circ}\text{C}.$ as the boiling point.

Technical cyclohexane was nitrated with 5 parts of concentrated nitric acid and 9 parts of concentrated sulfuric acid at $5\text{--}10^{\circ}\text{C}.$ for 6 hr., washed several times with water, with sodium hydroxide, and several times more with water, dried over calcium chloride, and then rectified. Four top and three bottom fractions were discarded. The freezing point of $6.41^{\circ}\text{C}.$, taken in the presence of calcium chloride, was lowered $0.08^{\circ}\text{C}.$ when about half was frozen, which indicates $6.49^{\circ}\text{C}.$ as the freezing point of pure cyclohexane. The depression of $0.08^{\circ}\text{C}.$ corresponds to 0.03 mole per cent of impurity detectable by freezing point depression. Our vapor pressure curve gives $80.74^{\circ}\text{C}.$ as the normal boiling point. Timmermans and Martin (20) give $6.50^{\circ}\text{C}.$ and $80.80^{\circ}\text{C}.$ as the freezing point and boiling point, respectively, of cyclohexane.

The method of determining the liquid-vapor equilibrium was the same

as that in paper I of this series (15), except that the trap was cooled with a carbon dioxide-ethyl alcohol slush for most of the measurements with mixtures. An error was discovered in the calibration of the thermocouple, so that the measurements had not been made at exactly even temperatures. Measurements of the vapor pressure of water were made at the same temperatures (potentiometer settings) as used for the vapor pressure measurements from 50° to 80°C., and a new calibration curve was made from the equation of Smith, Keyes, and Gerry (19) for the vapor pressure of water.

The vapor pressures of benzene and cyclohexane were measured at 5°C. intervals from 30° to 80°C. These measurements were fitted by least squares with the equations:

$$\log P_1 = 8.48882 - 2841.240/T + 4.97551 \times 10^5/T^2 - 6.84239 \times 10^7/T^3 \quad (1)$$

$$\log P_2 = 6.97180 - 1368.565/T + 9.293 \times 10^3/T^2 - 1.32146 \times 10^7/T^3 \quad (2)$$

($T = t + 273.16^\circ\text{C.}$) with standard deviations of 1.0×10^{-4} and 1.0×10^{-4} , which correspond to less than 0.01°C. in the temperature. The

TABLE 1
Vapor pressures of benzene and cyclohexane

<i>t</i>	<i>P</i> ₁ (BENZENE)	<i>P</i> ₂ (CYCLOHEXANE)
°C.	<i>mm.</i>	<i>mm.</i>
30	118.75	121.42
40	182.61	184.55
50	271.41	271.82
60	391.70	389.35
70	550.96	543.98
80	757.65	743.19

values of the pressures calculated at rounded temperatures are given in table 1.

The compositions of the equilibrium liquid and vapor were determined from measurements of the densities at 30°C. Table 2 contains the weight fraction of benzene, the observed density minus that calculated from the empirical equation given below, and the observed fractional change on mixing, V^M/V^0 . The equation used for the densities is

$$d = \frac{0.86836 - 0.09922z_2}{1 + 0.0243z_1z_2(1 + 0.288z_2^2)} \quad (3)$$

$$z_1 = 1 - z_2 = \frac{W_1/d_1}{W_1/d_1 + W_2/d_2} \quad (4)$$

in which W_1 is the weight of the benzene, d_1 is its density, and z_1 is its volume fraction, z_2 is the volume fraction of cyclohexane, etc. V is the volume of the mixture, V^0 the volume of the unmixed components at the

TABLE 2
Densities at 30°C.

WEIGHT FRACTION OF BENZENE	MOLE FRACTION OF BENZENE	DENSITY	DEVIATION FROM EQUATION 1	$100V^M/V^0$
0.0000	0.0000	0.76914		
0.1217	0.1299	0.77774	+0.00001	0.289
0.2339	0.2476	0.78648	-0.00001	0.481
0.3508	0.3680	0.79645	-0.00002	0.603
0.4843	0.5030	0.80892	+0.00001	0.652
0.6088	0.6264	0.82154	+0.00001	0.621
0.7483	0.7620	0.83689	-0.00001	0.497
0.8677	0.8761	0.85118	-0.00001	0.307
0.8679	0.8762	0.85124	+0.00003	0.302
1.0000	1.0000	0.86836		

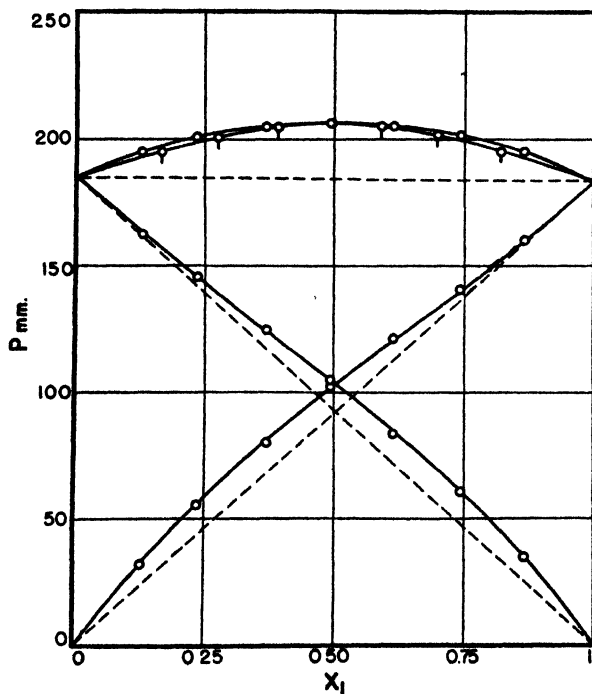


FIG. 1. Vapor pressure versus mole fraction for benzene-cyclohexane at 40°C.

same temperature and pressure, and $V^M = V - V^0$. From equation 3 it follows that

$$V^M/V^0 = 0.0243z_1z_2(1 + 0.288z_2^2) \quad (5)$$

The equation fits the measurements excellently. Since the density difference is about 0.1, the error of the determination of the composition should be about ten times as great as that in determining the density, or not more than 0.02 to 0.03 per cent.

Vapor-liquid equilibrium measurements with mixtures were made at intervals of approximately one-eighth in the mole fraction at 40° and at 70°C. and for a single mixture, about 50 mole per cent, at 30°, 50° and 60°C. The measurements are illustrated in figure 1, in which the curves are determined from equations 8, 9, 18, and 19. The top curve gives the liquid composition versus the equilibrium pressure, the curve just below it and the flagged circles give the vapor composition, and the two lower curves are the derived partial pressures versus the liquid composition. The broken lines are the Raoult's law lines for the total and the partial pressures. The measurements are reported in detail in table 3 as mole fraction of benzene in the liquid and in the vapor, equilibrium pressure, and the derived excess free energy of mixing. After each of the last three is given the deviation of the corresponding quantity from that calculated by equations 8, 9, 18, and 19. These deviations will be discussed later.

In paper II (16) it was shown that, if the liquid and vapor volumes are given, respectively, by

$$V/(N_1 + N_2) = V_1x_1 + V_2x_2 \quad (6)$$

and

$$V'/(N_1 + N_2) = RT/P + \beta_1y_1 + \beta_2y_2 \quad (7)$$

the excess chemical potentials and other excess thermodynamic functions are given by

$$\mu_1^E = RT \ln Py_1/P_1x_1 + (\beta_1 - V_1)(P - P_1) \quad (8)$$

$$\mu_2^E = RT \ln Py_2/P_2x_2 + (\beta_2 - V_2)(P - P_2) \quad (9)$$

$$F_x^E = F^E/(N_1 + N_2) = x_1\mu_1^E + x_2\mu_2^E \quad (10)$$

$$S_x^E = -(\partial F_x^E/\partial T)_{p,N} \quad (11)$$

$$H_x^M = F_x^E + TS_x^E \quad (12)$$

in which N_1 and N_2 are the numbers of moles of the two components, x_1 and x_2 are the mole fractions in the liquid, y_1 and y_2 are the mole fractions in the vapor, P is the vapor pressure of the solution, P_1 and P_2 are the vapor pressures of the components, V_1 and V_2 are the volumes of the liquid components, and β_1 and β_2 are functions of the temperature characteristic of each of the two substances. The effect on the subsequent equations of the error in equation 6 is entirely negligible. If the β 's combine quadratically, which should give an adequate approximation, the deviations from additive volume in the vapor which are ignored in equation 7 should give an effect of less than 0.05 per cent.

Measurements of β for benzene by Eucken and Mayer (1) from 60° to 100°C. are 0.9 as large as those calculated by the theory of corresponding states from the equation of Keyes, Smith, and Gerry (8) for water vapor (16). We have therefore taken 0.9 of the corresponding state value from

TABLE 3
Vapor pressures of mixtures

<i>t</i> °C.	MOLE FRACTION OF BENZENE		DEVIATION IN y_1	<i>P</i> mm.	DEVIATION IN <i>P</i>	P_x^E cal. per mole	DEVIATION IN P_x^E
	In liquid (x_1)	In vapor (y_1)					
39.99 ₇	0.1282	0.1657	-0.0028	194.94	-0.10	30.84	+0.14
	0.2354	0.2766	-0.0028	200.65	-0.12	49.82	-0.01
	0.3685	0.3912	-0.0048	204.75	-0.12	65.04	-0.06
	0.4932	0.4950	-0.0001	206.12	-0.03	70.65	-0.05
	0.6143	0.5909	+0.0012	205.18	-0.04	67.95	-0.10
	0.7428	0.6979	+0.0005	201.73	+0.08	56.14	-0.05
	0.8656	0.8205	+0.0013	195.04	-0.02	34.85	+0.15
69.98 ₀	0.1186	0.1486	-0.0023	567.60	-0.22	24.71	+0.10
	0.2409	0.2805	+0.0017	584.90	-0.02	43.20	-0.24
	0.3759	0.3982	-0.0031	596.16	+0.03	56.56	+0.22
	0.4945	0.4975	-0.0039	600.27	-0.62	60.04	-0.70
	0.6180	0.6027	-0.0004	599.32	+0.21	58.43	+0.24
	0.7248	0.6962	+0.0006	593.48	+0.15	50.25	+0.36
	0.8659	0.8311	-0.0024	577.79	+0.25	29.65	-0.10
29.98 ₆	0.4952	0.4948	+0.0008	136.38	+0.36	75.75	+1.57
49.99 ₂	0.4593	0.4680	-0.0020	302.07	-0.19	66.41	-0.38
59.95 ₃	0.4517	0.4649	+0.0003	430.28	-0.12	63.03	-0.22

Vapor pressures of the pure substances

TEMPERATURE	<i>P</i> ₁ (BENZENE)	<i>P</i> ₂ (CYCLOHEXANE)
°C.	mm.	mm.
29.98 ₆	118.67	121.35
39.99 ₇	182.59	184.51
49.99 ₂	271.38	271.76
59.95 ₃	391.06	388.81
69.98 ₀	550.63	543.58

water for both benzene and cyclohexane, using the critical data (5). As the increases in the vapor pressures are approximately proportional to the product x_1x_2 , this gas imperfection correction term in each chemical potential is also proportional to x_1x_2 . The two β 's are about equal, so

the correction to F_x^R also has this form. Since F_x^R itself is approximately of this form, the percentage correction changes little with the concentration; it varies from about 2 per cent at 30°C. to about 4 per cent at 70°C.

The simple theory referred to above leads to the following equation for the excess free energy per mole,

$$F_x^R = V_x^0 A_{12} z_1 z_2 \quad (13)$$

$$V_x^0 = x_1 V_1 + x_2 V_2 = V^0 / (N_1 + N_2) \quad (14)$$

in which A_{12} is independent of both the temperature and the composition. To fit our measurements it is necessary to make A_{12} a linear function of the temperature and of the square of the volume fraction of the cyclohexane,

$$F_x^R = (6.943 - 0.013233T) V_x^0 z_1 z_2 (1 + 0.084z_2^2) \quad (15)$$

in which F_x^R is in calories and $V_x^0 = 89.95 (1 + 0.2164x_2)$. It follows that

$$H_x^M = 6.943 V_x^0 z_1 z_2 (1 + 0.084z_2^2) \quad (16)$$

$$S_x^R = 0.013233 V_x^0 z_1 z_2 (1 + 0.084z_2^2) \quad (17)$$

$$\mu_1^R = (6.943 - 0.013233T) V_1 z_2^2 (1 - 0.168z_2 + 0.252z_2^2) \quad (18)$$

$$\mu_2^R = (6.943 - 0.013233T) V_2 z_1^2 (1 + 0.252z_2^2) \quad (19)$$

The calculated results from which the deviations in table 3 are calculated are from equation 15 for F_x^R , and the combination of equations 8, 9, 18, and 19 for P and y_1 .

The numerical constants are chosen to give the average of F_x^R for the measurements at 40°C. and at 70°C. and the assumption that F_x^R is linear in the temperature. The average error is about 0.2 per cent in y and 0.05 per cent in P except for the point at 30°C., where a larger error may be expected because the pressure is low for this type of apparatus. These deviations assume that the x measurements are exact, and this assumption is the only one which makes all the relations explicit. It is probably more in accord with the facts, however, to assume that the pressure is exact and to calculate x and y . Whenever the deviation we have found for P times dP/dy has the same sign as the deviation for y , this latter deviation will be divided between the x and y deviations if P is assumed exact. This relation holds for the ten cases of the fourteen at 40° and 70°C. which include the nine largest pressure deviations.

Schmitt (17) and Nagornov (11) have measured the total pressures of benzene-cyclohexane mixtures. Although Schmitt's pressures of the pure substances are lower than ours by a few millimeters, his pressures for the mixtures are all higher. Since he used a mercury thermometer and one

method of degassing for the pure substances and another for the mixtures, we attribute the first difference to the difference in temperature scales, and the second to the inefficiency of his second degassing method. He also measured the azeotropic composition as a function of the pressure. We confirm these measurements as closely as we can interpolate them. Nagornov's measurements of the total pressures are in excellent agreement with ours. In the abstracts in *Chemische Zentralblatt* and in *Chemical Abstracts*, however, 1253.9 should replace 1253.3 in the equation for 50.36% benzene.

Wolf, Frahm, and Harms (23, 24) present their measurements of the heat of mixing of benzene and cyclohexane only as a curve of H_x^M/x_1 . The curve appears to correspond to our H_x^M as to shape but to yield values from 12 to 15 per cent higher. The fact that our deviation in F_x^E is positive at 30°C. and negative at 50° and 60°C. indicates that the temperature relation is probably more complicated than that given. The equation

$$F_x^E = (13.154 - 0.051158T + 0.00005777T^2)V_x^0z_1z_2(1 + 0.084z_2^2) \quad (20)$$

gives a deviation in F_x^E of 1.13 cal. at 30°C., - 0.03 at 50°C., and + 0.03 at 60°C., and yields a value of H_x^M at 20°C. which agrees with the direct measurements within 1 per cent. This is the limit of accuracy with which we can read their curve. However, our measurements are not sufficiently accurate to warrant this more complicated expression, and the agreement with the directly measured heats may be fortuitous.

If the deviation from regularity be measured by the ratio

$$(H^M - F^E)/F^E$$

these solutions are very far from regular, for this ratio, which is 0 for a regular solution, is 1.37 at 30°C., and 1.89 at 70°C. One of us has shown elsewhere (14) that the theory should lead to the ideal entropy of mixing for the process in which the total volume is kept constant rather than for the constant pressure process, and has calculated the differences between the appropriate thermodynamic functions for the two cases. We shall carry out the computations for 30°C., since the auxiliary data needed for the computations are better known at that temperature. For the coefficients of thermal expansion and of compressibility (6) of the unmixed liquids we use

$$\alpha_0 = 1.225 (1 - 0.058z_2) \times 10^{-3}$$

$$\beta_0 = 1.02 (1 + 0.12z_2) \times 10^{-4}$$

and we assume, for lack of measurements except on benzene (6), that $(d \ln \beta)/dT$ is independent of the composition and equal to 0.0076; an approximate value for this quantity is quite sufficient. We shall use the sub-

script p to indicate the change for the constant pressure process and the subscript v to indicate the change at constant volume. Then

$$A_v^E - F_p^E = (V^0/2\beta)(V^M/V^0)^2$$

$$(A_v^E - F_p^E)_x = \frac{0.0701[89.95(1 + 0.2146x_2)](1 + 0.288z_2^2)z_1^2z_2^2}{1 + 0.12z_2} \quad (21)$$

$$S_v^E - S_p^E = -V^M\alpha_0/\beta_0 + \frac{V^0 \ln \beta}{2\beta dT} (V^M/V^0)^2$$

$$(S_v^E - S_p^E)_x = -0.00707[89.95(1 + 0.2146x_2)](1 + 0.288z_2^2)(1 - 0.15926z_2)z_1z_2$$

$$+ \frac{d \ln \beta}{dT} (A_v^E - F_p^E)_x \quad (22)^3$$

so that

$$E_v^M - H_p^M = -V^M T\alpha_0/\beta_0 + \frac{V^0}{\beta} \left(1 + \frac{d \ln \beta}{d \ln T}\right) (V^M/V^0)^2$$

$$(E_v^M - H_p^M)_x = T(S_v^E - S_p^E)_x + (A_v^E - F_p^E)_x \quad (23)$$

In figure 2 are shown F_{px}^E at 30°C. and at 70°C. from equation 15 to show the variation in this quantity, H_{px}^M from equation 16, and E_{vx}^M at 30°C. calculated from H_{px}^M and equation 22. The difference between A_{vx}^E and F_{px}^E at 30°C. is about half the width of the line, so that one curve may represent either function. TS_{px}^E is the difference between the top curve and the third, and TS_{vx}^E is the difference between the second and third curves. It may be seen that the latter is slightly less than half the former, so that half of the deviation from regularity is accounted for by the change in volume on mixing.

The most obvious contribution to the S_x^E is that which arises from the difference in cohesive energies causing a molecule to have on the average more neighbors of its own species than it would have with random distribution. This contribution has been worked out for spheres of equal sizes by Guggenheim (2, 3), Rushbrooke (12), and Kirkwood (9). The last two are in essential agreement, so we will take Kirkwood's value, and assume eight nearest neighbors. For spheres of equal radii whose excess energy per mole is 120 cal. in the equimolar mixture this gives, in our notation,

$$E_{vx}^M = B_{12}x_1x_2 - (B_{12}^2/4RT)x_1^2x_2^2 \quad (24)$$

$$120 = B_{12}/4 - B_{12}^2/64RT$$

$$B_{12} = 507$$

$$E_{vx}^M - A_{vx}^E = (-B_{12}^2/8RT)x_1^2x_2^2 \quad (25)$$

$$= -3.6 \text{ cal.}, \text{ when } x_1 = 0.5$$

³ The errors in the corresponding equation in reference 14 are corrected here.

We may probably apply these results to the benzene-cyclohexane system to the extent that we may say that this deviation from random distribution gives a negative entropy which is 5 to 10 per cent of the positive entropy we must explain. We may be sure that it leads to a negative entropy.⁴

It is difficult to picture a positive excess entropy in terms of randomness, for the ideal entropy increase corresponds to complete randomness of position. It seems to us that the most probable explanation is that the pure components have not complete randomness of orientation, and that the orientation becomes more random on mixing. From the crystal structure of the two components (7), we might expect that in either liquid

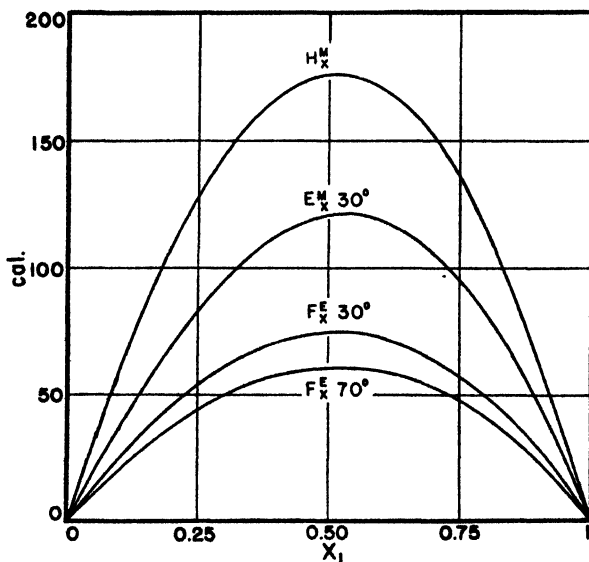


FIG. 2. Various thermodynamic functions for benzene-cyclohexane

two neighbors would favor the position in which the planes of their carbon atoms are mutually perpendicular. If this position is less favored when one neighbor is benzene and the other cyclohexane there will be a positive excess entropy of mixing. The tendency for favored positions need not be great, for the maximum excess entropy at constant volume is 0.15 cal. per mole °C.

⁴ It will be recalled that this system is the one for which Ward (21) found evidence of emulsoid structure from the fact that the peaks characteristic of the components persist in the x-ray spectrum of the mixtures. Warren and Murray (22) have repeated these measurements and find no evidence of two peaks. They also show that the peaks of benzene and cyclohexane are so close that they must show as a single peak for the mixtures, even if the mixture were completely emulsoid, so that x-rays cannot answer this question. For such emulsoid mixtures the ideal entropy of mixing would practically disappear, giving for the equimolal mixture a difference ($E_{xx}^M - A_{xx}^E$) of about 800 cal., which seems entirely impossible.

It is possible that the asymmetry expressed as $(1 + 0.084z_2^2)$, etc., has a similar explanation. The computation of E_v^M and S_v^E includes all the uncertainties of our own and other measurements, but it does appear probable that the asymmetry term in E_v^M is small or has the opposite sign to that in F_p^E , and that the asymmetry term in S_v^E is about equal to that in V^M , $(1 + 0.288z_2^2)$, and therefore much larger than that in F_p^E . If the cyclohexane molecules have a very slight tendency to favor the crystal lattice in the liquid, so that in solutions consisting largely of cyclohexane the other molecules are unable to utilize all the space left free when one cyclohexane molecule is replaced by a smaller benzene molecule, but in solutions consisting largely of benzene each cyclohexane molecule requires the same volume as in cyclohexane, then there would be an asymmetry of this sign in the volume. Accurate measurements of the volume of benzene-cyclohexane mixtures over a range of temperature and pressure should be of great interest in this connection.

If the cohesive energy density, $a = (E - E_0)/V$, is equal to $-(\partial E/\partial V)_T$ and S_v^E is zero, E_v^M may be computed from V^M and $\beta_0(14)$,

$$E_v^M = V^M/\beta_0 \quad (26)$$

The first assumption is approximately true for this system, but we have just shown that the second is not. For the equimolal mixture E_v^M so calculated is 161 cal. per mole, which comes nearer the measured H_p^M value, 175.5, than the measured E_v^M value, 120.0.

From equations 1 and 2 for the vapor pressures of the components and from their densities at 30°C., the cohesive energy densities of the components, corrected for the deviations from the perfect gas laws, are calculated as $a_{11} = -83.67$ and $a_{22} = -66.49$ cal. per cubic centimeter. The assumption that the mutual energy per unit volumes, a_{12} , is equal to $\sqrt{a_{11}a_{22}}$ leads to

$$A_{12} = -(\sqrt{a_{11}} - \sqrt{a_{22}})^2$$

With the equation

$$E_v^M/V^0 = A_{12}z_1z_2$$

this leads to $E_v^M = 26$ cal. per mole for the equimolal mixture, which is very much smaller than the measured 120 cal. However, if the calculation is reversed and a_{12} is calculated from the relation

$$A_{12} = 2a_{12} - a_{11} - a_{22}$$

the value -72.72 is obtained, which is only 2.5 per cent less than $\sqrt{a_{11}a_{22}} = -74.59$. So the quadratic combination gives a good approximation for the mutual energy, and the small error is in the direction predicted by the quantum theory (10), but the solution theory requires a small difference between large quantities, which magnifies the relative error enormously.

SUMMARY

The vapor-liquid equilibrium of benzene-cyclohexane mixtures has been measured at 40° and 70°C. over the whole composition range, and at 30°, 50°, and 60°C. for approximately equimolal mixtures. The densities of the liquid mixtures have been measured at 30°C. The measurements have been expressed analytically.

From these measurements have been calculated the thermodynamic functions, including the energy and entropy of mixing at constant total volume.

These mixtures are very far from regular, and only half the deviation is explained by the volume change on mixing. There is also an asymmetry in the relation to composition.

It is suggested that these facts may be explained by the persistence in the pure liquids of a slight tendency toward the orientations of the crystal lattices.

REFERENCES

- (1) FUCKEN, A., AND MAYER, L.: *Z. physik. Chem.* **B5**, 452 (1929).
- (2) GUGGENHEIM, E. A.: *Proc. Roy. Soc. (London)* **A148**, 304 (1935).
- (3) GUGGENHEIM, E. A.: In *Fowler's Statistical Mechanics*, 2nd edition, p. 535. University Press, Cambridge (1936).
- (4) HILDEBRAND, J. H., AND WOOD, S. E.: *J. Chem. Phys.* **1**, 817 (1933).
- (5) *International Critical Tables*, Vol. III, p. 244. McGraw-Hill Book Co., Inc., New York (1928).
- (6) *International Critical Tables*, Vol. III, pp. 29, 39. McGraw-Hill Book Co., Inc., New York (1928).
- (7) KATZOFF, S.: *J. Chem. Phys.* **2**, 841 (1934).
- (8) KEYES, F. G., SMITH, L. B., AND GERRY, H. T.: *Proc. Am. Acad. Arts Sci.* **70**, 319 (1936).
- (9) KIRKWOOD, J. G.: *J. Phys. Chem.* **43**, 97 (1939).
- (10) LONDON, F.: *Z. physik. Chem.* **B11**, 222 (1930).
- (11) NAGORNOV, N. N.: *Ann. inst. anal. phys. chem. (U. S. S. R)* **3**, 562 (1927).
- (12) RUSHBROOKE, G. S.: *Proc. Roy. Soc. (London)* **A166**, 296 (1938).
- (13) SCATCHARD, G.: *Chem. Rev.* **8**, 321 (1931).
- (14) SCATCHARD, G.: *Trans. Faraday Soc.* **33**, 160 (1937).
- (15) SCATCHARD, G., RAYMOND, C. L., AND GILMANN, H. H.: *J. Am. Chem. Soc.* **60**, 1275 (1938).
- (16) SCATCHARD, G., AND RAYMOND, C. L.: *J. Am. Chem. Soc.* **60**, 1278 (1938).
- (17) SCHMITT, M.: *Publications scientifiques et techniques du ministère de l'air (France)*, **54** (1934).
- (18) SMITH, E. R., AND MATHESON, H.: *J. Research Natl. Bur. Standards* **20**, 641 (1938).
- (19) SMITH, L. B., KEYES, F. G., AND GERRY, H. T.: *Proc. Am. Acad. Arts Sci.* **69**, 137 (1934).
- (20) TIMMERMANS, J., AND MARTIN, F.: *J. chim. phys.* **23**, 750 (1926).
- (21) WARD, H. K.: *J. Chem. Phys.* **2**, 153 (1934).
- (22) WARREN, B. E., AND MURRAY, G. E.: *Personal communication*.
- (23) WOLF, K. L.: *Trans. Faraday Soc.* **33**, 179 (1937).
- (24) WOLF, K. L., FRAHM, H., AND HARMS, H.: *Z. physik. Chem.* **B36**, 260 (1937).

THE EFFECT OF INTERMOLECULAR ACTION UPON DIELECTRIC POLARIZATION¹

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In the early days of dipole moment investigations, it was shown that the Debye equation (1) for the dielectric constant applied not only to gases but also approximately to very dilute solutions of polar molecules in a non-polar solvent, measurements being carried out over a range of concentration to permit of extrapolation to infinite dilution and over a wide range of temperature to establish the linearity of the relation between the polarization and the reciprocal of the absolute temperature (12, 13, 14). The familiar equation underlying these investigations is

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3} \alpha_0 + \frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT} \quad (1)$$

in which P = the molar polarization,

ϵ = the dielectric constant,

M = the molecular weight,

d = the density,

N = the number of molecules per mole, 6.023×10^{23} ,

α_0 = the molecular polarizability,

μ = the permanent dipole moment of the molecule,

k = the Boltzmann constant, 1.380×10^{-16} , and

T = the absolute temperature.

If a polar substance 2 of moment μ is dissolved in a non-polar liquid 1, for which $\mu = 0$, the molar polarization P_{12} of the mixture, its dielectric constant ϵ , and its density d are related by the expression

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{c_1 M_1 + c_2 M_2}{d} = c_1 P_1 + c_2 P_2 \quad (2)$$

in which c_1 and c_2 are the mole fractions of substances 1 and 2, the subscript 2 being used as in subsequent equations in this paper to refer to the

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substance having a permanent dipole in its molecule. As a not bad approximation, P_1 may be assumed to retain the value that it has for the pure substance 1. P_2 can then be calculated as

$$P_2 = P_1 + (P_{12} - P_1)/c_2 \quad (3)$$

The decrease in P_2 , the polarization of the polar substance, commonly found to occur with increasing c_2 , that is, increasing dipole concentration, was attributed by some investigators to molecular association into actual complexes in which the dipoles opposed one another (16), and the equilibria supposed to exist between these complex molecules and the single molecules were calculated from the polarization values. Although it seemed necessary,—and still does seem so,—to suppose actual complex formation to occur in the alcohols and fatty acids, where we now know that hydrogen bonds may attach two or more molecules to one another, it appeared more reasonable to attribute the effect to a more or less loose intermolecular orientating effect, of which the complex formation with alcohols was an extreme case (13, 16). This orientating effect was seen to be larger, the larger the dipoles and the less their separation or insulation from neighboring dipoles (14). Since these experimental investigations were carried out and their qualitative interpretation suggested, many quantitative treatments of the effects of intermolecular action upon apparent dipole moment and polarization have been attempted. It is not the purpose of this paper to review these attempts, but rather to examine in the light of these treatments the earlier experimental data obtained in this laboratory on a group of related substances of now well-known molecular structures. It is hoped that this examination may throw light upon some very typical dielectric behavior and show the value as well as the limitations of the theoretical treatments.

Although from the first it was recognized that there must be some interaction between polar solute molecules and non-polar molecules of solvent surrounding them, the differences observed experimentally between the few moment values obtained in different solvents and in the vapor state were of the magnitude of the possible experimental error. Müller's systematic experimental investigation (8) of a large number of very dilute solutions showed a dependence of the apparent value of the moment obtained from the polarization extrapolated to infinite dilution upon the dielectric constant of the solvent, a considerable number of molecules giving values which could be represented by a single empirical equation, although some substances, such as the alcohols, behaved differently. Frank (5) and Higasi (7) have independently shown that this behavior may depend largely upon the internal polarizabilities of the molecules, which are averaged as α_0 in the Debye equation, and upon the positions of the axes of these polarizabilities relative to those of the dipoles. As

Higasi has demonstrated the approximate applicability of his treatment to a considerable number of substances, the details of the present discussion will be concerned primarily with intermolecular action in more concentrated solutions, such as those used in the majority of the earlier measurements in this laboratory.

In many of the theoretical treatments, the polarization is expressed as the polarization per cm.³, $(\epsilon - 1)/(\epsilon + 2)$, which may be converted to P , the polarization per mole, by multiplying by the molar volume M/d . In what follows, this conversion is made in the various equations examined, since the experimental data are commonly expressed in terms of molar polarization. P may be written

$$P = P_E + P_A + P_M \quad (4)$$

where P_E is the electronic polarization given by the molar refraction, P_A is the small atomic polarization, and P_M is the moment or orientation polarization, which is the polarization arising from the orientation of the permanent dipoles in an externally applied field. The induced polarization,

$$P_E + P_A = \frac{4\pi N}{3} \alpha_0 \quad (5)$$

varies so little with temperature and concentration that it will be treated as constant in the present discussion and subtracted from P to obtain the moment or orientation polarization,

$$P_M = \frac{4\pi N}{3} \frac{\mu^2}{3kT} \quad (6)$$

van Arkel and Snoek (20) have modified this expression in the Debye equation in a semi-empirical fashion by the introduction into the denominator of an additional energy term $cn\mu^2$ to give

$$P_M = \frac{4\pi N}{3} \frac{\mu^2}{(3kT + cn\mu^2)} \quad (7)$$

in which n is the number of dipole molecules per cm.³ and c is a constant, which they declare to be quite independent of n , independent of the nature of the solvent, and largely independent of the nature of the dipole molecule, although it may vary greatly for a substance which is associated.

They have tabulated values of $\frac{3}{4\pi} c$, instead of the c actually used in their equation, for twenty-three substances, the values, with the exception of one of doubtful accuracy, lying between 1.0 and 1.7 and tending to lie about halfway between these limits, that is, near 1.35. The highly asso-

ciated alcohols give negative values; nitriles give values which vary with concentration and with solvent, the variation being attributed to molecular association.

Müller (9) has recently examined this van Arkel and Snoek equation in terms of the Debye theory of hindered rotation (3), which gives

$$P_M = \frac{4\pi N}{3} \frac{\mu^2}{3kT} R(y) \quad (8)$$

where $y = E/kT$, E being the variation in the potential energy of the molecules when they rotate through an angle 2π , or, in other words, the height of the potential energy hump which has to be passed over for complete rotation. The function $R(y)$ is given by

$$R(y) = 1 - L^2(y) \quad (9)$$

and the Langevin function $L(y)$ by

$$L(y) = \coth y - 1/y \quad (10)$$

In the case of very strong dipole interaction $3kT$ can be neglected in the van Arkel and Snoek equation in comparison with $cn\mu^2$, an approximation which, in combination with the development of $R(y)$ for large y , gives

$$E = 2/3 \, cn\mu^2 \quad (11)$$

For dilute solutions Müller's treatment leads to an expression

$$E = E_0 + \frac{\beta n\mu^2}{2E_0 kT} \quad (12)$$

although Müller has omitted the E_0 from the denominator of the second term on the right. Instead of this one may write

$$E^2 = E_0^2 + \frac{\beta n\mu^2}{kT} \quad (13)$$

in which E_0 is evidently the value of E for infinite dilution, that is, a potential energy arising wholly from the presence of solvent molecules around those of the solute. β is given by the expression

$$\beta = \frac{81}{4\pi N} \left(\frac{kT}{\mu} \right)^4 \frac{\delta P_2}{\delta n} \quad (14)$$

which is obtained experimentally, $\delta P_2/\delta n$ being treated as independent of concentration, an approximation usually justified only in very dilute solutions. van Arkel and Snoek (20) have shown that their equation represents closely the behavior of nitrobenzene over a wide range of concentra-

tion in four different solvents and at temperatures between 22°C. and 100°C. and fairly well that of pure chlorobenzene from -50°C. to 70°C. observed in this laboratory (12). Müller (9) finds that the van Arkel equation represents the variation of the polarizations of nitrobenzene in carbon tetrachloride and of chlorobenzene in hexane fairly well and better than does the Debye equation modified for restricted rotation. He finds also that c , calculated from data on chlorobenzene at high pressures, increases about 8 per cent as the pressure increases from 1 to 8000 atm., while c for liquid sulfur dioxide is independent of temperature through a range of about 100°C. until it approaches the critical temperature, when it decreases rapidly, presumably reaching zero at the critical temperature. Because of the apparent closeness with which the van Arkel equation seems capable of representing experimental data and of the physical significance which Müller's work has given to the constant c of this equation, it is selected here for use in the detailed examination of earlier experimental data obtained in this laboratory.

As accurate values have been obtained for the moment and for $P_E + P_A$ of ethyl bromide in the vapor state (17), it is a particularly good substance to examine in detail. The values of $\frac{3}{4\pi}c$ are calculated from the rearranged equation of van Arkel and Snoek

$$\frac{3}{4\pi}c = \frac{M}{d} \left(\frac{1}{P_M} - \frac{9kT}{4\pi N\mu^2} \right) \quad (15)$$

The values for pure ethyl bromide (table 1) are higher than that originally calculated by van Arkel and Snoek from the same data for the liquid, presumably because of a higher value used for the moment. c decreases uniformly with rising temperature, being 10 per cent lower at 30°C. than at -90°C. When ethyl bromide is diluted with hexane, c increases but slightly until c_2 falls below 0.5 when it changes with increasing rapidity, being three times as great at $c_2 = 0.0309$ as in the pure liquid (table 2). The reason that the values of c vary so much in dilute solution while the polarization values calculated by means of the c for the pure liquid are fairly close to the observed is that the differences between the polarizations observed in dilute solutions and those in the vapor state are not large. Consequently, a considerable change in c does not greatly alter the polarization in dilute solution. Conversely, a small difference in the polarization in dilute solution has a large effect upon the value calculated for c .

According to the original derivation of van Arkel and Snoek as well as the further development of Müller, c is a proportionality factor connecting the energy of the molecular interaction with the concentration of the dipoles and the square of their moments. If the dipole molecules were spherical with the dipoles located at their centers, and if they did not in-

TABLE 1
Variation of van Arkel constant with temperature

C ₂ H ₅ Br				n-C ₇ H ₁₆ Br			
$\mu(\times 10^{18}) = 2.02$ $P_E + P_A = 21.5$				$\mu(\times 10^{18}) = 2.07(18)$ $P_E + P_A = 45.8$			
t in °C.	$\frac{4\pi N\mu^2}{9kT}$	P_M	$\frac{3}{4\pi} c$	t in °C.	$\frac{4\pi N\mu^2}{9kT}$	P_M	$\frac{3}{4\pi} c$
-90	135.8	32.7	1.49	-70	128.7	52.7	1.62
-70	122.5	32.9	1.46	-50	117.1	51.7	1.59
-50	111.5	33.0	1.43	-30	107.5	50.5	1.57
-30	102.3	33.2	1.41	-10	99.5	49.3	1.56
-10	94.6	33.3	1.38	10	92.5	48.2	1.54
10	87.9	33.5	1.35	30	86.4	47.2	1.52
30	82.0	33.6	1.32	50	81.1	46.3	1.49
50				70	76.4	45.5	1.46
70				90	72.1	44.7	1.43
90							

CHCl ₃				CHBr ₃			
$\mu(\times 10^{18}) = 1.15(6)$ $P_E + P_A = 23.0$				$\mu(\times 10^{18}) = 0.99$ $P_E + P_A = 32$			
t in °C.	$\frac{4\pi N\mu^2}{9kT}$	P_M	$\frac{3}{4\pi} c$	t in °C.	$\frac{4\pi N\mu^2}{kT}$	P_M	$\frac{3}{4\pi} c$
-50	36.1	24.4	0.98				
-30	33.2	23.5	0.93				
-10	30.6	22.8	0.88				
10	28.5	22.0	0.81	10	21.1	14.05	2.06
30	26.6	21.3	0.75	40	19.1	13.17	2.10
50	24.9	20.6	0.67	70	17.4	12.37	2.10

TABLE 2
Variation of van Arkel constant for ethyl bromide with concentration

c_2	P_M		$\frac{3}{4\pi} c$	
	-90°C.	30°C.	-90°C.	30°C.
0.0309	113.7	75.8	5.08	4.07
0.0783	103.6	72.4	3.00	2.54
0.1767	90.6	65.8	2.13	2.02
0.3395	74.0	59.2	1.72	1.53
0.5073	60.8	52.1	1.54	1.38
0.7188	47.4	43.7	1.48	1.35
1.000	32.7	33.6	1.49	1.33

teract in any way with the solvent molecules, one might expect c to be constant for a given solvent, although it should depend upon the dielectric constant of the solvent. The variation of c with solute, solvent, tempera-

ture, and concentration might be expected to be a measure of the departure from these unattainable ideal conditions. Müller attributed the rough constancy of c to the very large internal fields, millions of volts per centimeter, surrounding the molecules and producing saturation effects scarcely influenced by temperature. His value of c for sulfur dioxide was, however, only two-thirds that for chlorobenzene. The fact that c has much the same value for many different substances in the liquid state indicates that these liquids, insofar as they may be said to have structures, do not differ greatly from one another in structure, and that the dipole interaction is the predominant factor in lowering the polarization of the liquid below that of the vapor. The dipole interaction expressed by $cn\mu^2$ is so strong in liquid ethyl bromide that it is only after half of the ethyl bromide molecules have been replaced by hexane molecules that the apparent value of c begins to change to any considerable extent. Here the interaction between the solute and solvent molecules, which does not enter into the term $cn\mu^2$, begins to play an increasingly important part, causing an increase in the apparent values calculated for c . The increasing amount of molecular rotation with rising temperature should tend to decrease the molecular interaction and, hence, the value of c , as observed for ethyl bromide. These two effects thus qualitatively described are apparent in the expression for E (equation 12) for dilute solutions. The second term of this equation is proportional to that from which c is calculated. It should evidently decrease with rising temperature if β is constant, as Müller's investigations indicate it to be, and should, therefore, give rise to a decrease in the value of c with rising temperature. Since the first term E_0 becomes of increasing importance in comparison with the second term as the latter decreases with decreasing n , neglect of it results in an increase in the apparent value of c . To obtain an idea of the relative magnitudes of the two energies, E may be calculated from equation 8, developed and rearranged to give

$$E = 3kT(1 - 9kTP_M/4\pi N\mu^2)^{1/2} \quad (16)$$

The value of E thus obtained for the 0.0309 mole fraction solution of ethyl bromide in hexane at -90°C . is 3.07×10^{-14} ergs per molecule, while the value of E_0 obtained by the use of equation 13 is 2.39×10^{-14} , showing that only 0.68×10^{-14} erg of the total potential energy hump is due to the interaction between the dipoles in this dilute solution. The value of $\frac{3}{4\pi}c$ calculated for this solution in table 2 might be very roughly corrected by multiplying by 0.68/3.07 to obtain 1.13, as compared to 1.51 for pure ethyl bromide.

It is apparent that the variation of c for ethyl bromide is no more than might be expected. It may be added that when ethyl bromide was originally investigated (12), it was noted that intermolecular action in the pure

liquid was so strong as to reverse the normal decrease of polarization with rising temperature. Increase in the size of the halogen or of the alkyl group in the molecule was found to decrease this intermolecular action by increasing the insulation of the dipoles from one another, or, in terms of the present discussion, increase in molecular size decreases the number of molecules per cm^3 and, consequently, the term $cn\mu^2$, which measures the intermolecular action. If the shape of the molecule played an important rôle in restricting the molecular rotation, one would expect the value of c for *n*-heptyl bromide to be much larger than that of ethyl bromide, unless its long carbon chain is curled up in the liquid so as not to hinder the rotation of the molecule. Actually, the values of c found for heptyl bromide are somewhat, but not much, larger than those of ethyl bromide and vary in much the same way. The difference between the two may be accounted for by the smaller value of n , which makes the energy of the interaction with the solvent molecules more important and the error due to its neglect correspondingly greater. The value of c for tertiary butyl chloride, the molecule of which has the shape of a tetrahedron so rounded at the corners as to approach a sphere, differs little from the values for the normal butyl halides, which are close to those for ethyl and heptyl bromides. Insofar as the value of c may be regarded as giving any information concerning the restriction of rotation, one may conclude that the freedom of rotation of these molecules in the liquid is little affected by their shapes. In other words, steric hindrance has little effect in restricting their rotations. Such behavior contrasts strongly with that of molecular rotation in solids which is greatly influenced by molecular shape (19). The as yet unpublished measurements of Mr. W. O. Baker in this laboratory show, for example, that the molecules of the tertiary butyl halides, which are not far from spherical in form, rotate for some distance below the freezing point, while the normal butyl halides lose their molecular rotation on solidification.

The polarization of ethyl ether is practically independent of its concentration in solution and differs from that in the vapor state by no more than the experimental error, which gives a zero value to c for it. Because of the fairly large size of the molecule and the rather small size of its moment $n\mu^2$ is small, so that any calculation of c is subject to a considerable error. This is apparent in the values calculated for c for chloroform and bromoform. When 1.05×10^{-18} , the value obtained by solution measurements in the writer's laboratory (12), which is higher than the gas value 0.95×10^{-18} obtained by Sanger (11), was used in the calculation of c for chloroform, the values of c for the pure liquid started at a low value just above the freezing point and decreased through zero to a small negative value near the boiling point. When, however, the value 1.15×10^{-18} (6) was used, the values of c (table 1), although still small, did not decrease to zero. The measurements on bromoform were less accurate because of

its tendency to decompose, and the small and slightly uncertain values of $n\mu^2$ make the values obtained for $\frac{3}{4\pi}c$ at three temperatures (table 1) much more uncertain than they appear. It appears fairly certain, however, that c is larger than for chloroform and of about the usual magnitude. The inductive interaction between the solute and solvent molecules calculated by Higasi (7) and Frank (5) commonly lowers the polarization and will thus be lumped in with E_0 in giving too high an apparent value for c in dilute solutions.

When these measurements over a range of temperature were originally carried out in this laboratory, it was noted with surprise that, although the polarization values of the pure polar liquids were reduced by intermolecular action far below the values at infinite dilution, they were still linearly dependent upon the reciprocal of the absolute temperature (12). This linearity follows approximately from the van Arkel equation if both sides of the latter are inverted to give

$$\frac{1}{P_M} = \frac{9k}{4\pi N\mu^2} T + \frac{3cn}{4\pi N} \quad (17)$$

or

$$\frac{1}{P_M} = \frac{9k}{4\pi N\mu^2} T + \frac{3c}{4\pi M} d \quad (18)$$

The first term on the right is a constant times T and the second term a supposed constant times d , which, as a first approximation, is a linear function of T . The small decrease observed for c with increasing T is not sufficient to destroy the approximate linearity of the relation of $1/P_M$ to T . We thus see that the equation of van Arkel and Snoek, taken in conjunction with the Debye theory of restricted rotation as developed and applied by Müller, gives a plausible picture and an almost quantitative representation of the effect of intermolecular action upon dielectric polarization.

A totally different approach to the problem has been developed by Onsager (10) and further examined by Van Vleck (21) and by Cole (1). Considering the inductive interaction between molecules, Onsager derived an equation for pure polar liquids which may be written

$$P_M = \frac{4\pi N\mu^2}{9kT} f \quad (19)$$

where

$$f = \frac{3\epsilon(n^2 + 2)}{(2\epsilon + n^2)(\epsilon + 2)} \quad (20)$$

in which n is the refractive index. He showed that, for large values of ϵ and reasonable values of n , this equation could be simplified into an equation identical with an empirical relation found by Wyman (22) to have general, though extremely approximate, applicability to unassociated liquids. Application of the unsimplified equation to the previously considered data on pure ethyl bromide gives the unsatisfactory agreement shown in table 3, in which the values of n^2 are obtained by setting

$$P_E + P_A = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

The calculated reduction in the polarization is in the right direction but is not large enough. Cole (1), using an approximation justifiable when ϵ is

TABLE 3
Polarization values of ethyl bromide calculated from Onsager equation

t in $^{\circ}\text{C}.$	n^2	f	P_M (OBSERVED)	P_M (CALCULATED)
-90	2.48	0.346	32.7	47.3
-70	2.45	0.372	32.9	46.5
-50	2.395	0.404	33.0	45.0
-30	2.33	0.430	33.2	44.0
-10	2.285	0.456	33.3	43.1
10	2.24	0.483	33.5	42.5
30	2.19	0.511	33.6	41.8

large, simplifies f , introduces a factor q , and writes the Onsager equation in a form equivalent to

$$P_M - \frac{4\pi N\mu^2}{9kT} = q \left[\frac{3(n^2 + 2)}{2(\epsilon + 2)} - 1 \right] \cdot \frac{4\pi N\mu^2}{9kT} \quad (21)$$

The so-called local field parameter q , which Van Vleck gives as

$$q = 1 + (3\alpha kT/\mu^2) \quad (22)$$

is given as $0 \leq q \leq 1$ and used as an empirical constant necessary to make the original Onsager equation fit the experimental data compiled by Wyman. For the alcohols and water, which are unfitted by their strong molecular association for testing a general equation, the values of q vary from just below zero almost to 1. For the other substances, Cole finds values of q lying in the general vicinity of 1. The values of q calculated for ethyl bromide from its polarizability and moment are 1.05 at $-90^{\circ}\text{C}.$ and 1.09 at $30^{\circ}\text{C}.$ Comparison of the Cole equation with that of van Arkel and Snoek leads to an equation for the van Arkel c

$$\frac{3}{4\pi} c = \frac{(q(n^2 + 2) \cdot 4\pi N\mu^2/9kT) - q}{(2 + q) \cdot 4\pi N\mu^2/9kT} \quad (23)$$

If $q = 1$, the equation of Cole reduces to that of Onsager and

$$\frac{3}{4\pi} c = \frac{n^2 + 2}{3} - \frac{3kT}{4\pi N\mu^2} \cdot \frac{M}{d} \quad (24)$$

Application of this equation to ethyl bromide gives $\frac{3}{4\pi} c = 1.32$ at -90°C . and 1.06 at 30°C ., as compared to 1.49 and 1.32 obtained by direct application of the van Arkel equation to the experimental data (table 1). This discrepancy is a measure of the previously noted failure of the Onsager reduction factor f to reduce the calculated values of P_M down to the observed.

It may be pointed out in passing that Onsager's conclusion that "the formation of a 'hydrogen bond' increases the electric moment of the group which carries the hydrogen" can be interpreted satisfactorily in the light of complex formation without any change in bond moment (16). If, for instance, N molecules possessing dipole moment μ polymerize to form $N/2$ double molecules in which the two dipoles point in the same direction to give moment 2μ to each of the double molecules, the apparent value of P_M will double and the value calculated for the moment without consideration of these changes will be $\sqrt{2}\mu$, although no change in bond moment will necessarily have occurred.

The two general approaches to the problem of the effect of intermolecular action upon polarization lead to a factor or term which reduces the polarization below that which the substance would have in the vapor state. In one, the factor is obtained through the height of a potential energy hump which is adjusted to fit the data and gives a very plausible explanation and an almost quantitative representation of the experimental facts. The same general idea of restricted molecular rotation has been employed by Eyring and Kincaid (4) and, if consistency with the potential humps indicated by other physical properties is obtained, the validity of the general picture should be more definitely established. In the other approach, the factor as obtained by Onsager through consideration of induction between the molecules involves definite fixed physical constants, which are sufficient to give only a rough approximation to the experimental facts. The necessity of introducing a more or less adjustable modifying factor renders the significance of the agreement with experiment no greater than that in the case of the other method. The two approaches to the problem do not appear to be mutually exclusive.

SUMMARY

Previously determined values of dielectric polarization are examined in the light of the theory of restricted molecular rotation and of that of the modifying effect of a dipole on its surrounding medium. The variation

of these polarizations with temperature and concentration in solution is satisfactorily explained by the theory of restricted molecular rotation, as developed by Müller from the theory of Debye and the semi-empirical equation of van Arkel and Snoek. The equation developed by Onsager, taking account of the inductive effect of the dipoles upon the surrounding molecules, gives calculated polarization values not far from the observed but it must be modified by an adjustable factor, as proposed by Cole in accordance with a suggestion of Van Vleck, in order to fit the experimental facts closely.

REFERENCES

- (1) COLE: J. Chem. Phys. **6**, 385 (1938).
- (2) DEBYE: Physik. Z. **13**, 97 (1912).
- (3) DEBYE: Physik. Z. **36**, 100, 193 (1935); Chem. Rev. **19**, 171 (1936).
- (4) EYRING AND KINCAID: J. Chem. Phys. **6**, 620 (1938).
- (5) FRANK: Proc. Roy. Soc. (London) **A152**, 171 (1935).
- (6) FUCHS AND WOLF: Appendix, "Dielektrische Polarisation," in Hand- und Jahrbuch der chemischen Physik. Akademische Verlagsgesellschaft, M.B.H., Leipzig (1935).
- (7) HIGASI: Sci. Papers Inst. Phys. Chem. Research (Tokyo) **28**, 284 (1936).
- (8) MÜLLER: Physik. Z. **34**, 689 (1933); **35**, 346 (1934).
- (9) MÜLLER: Physik. Z. **38**, 498 (1937).
- (10) ONSAGER: J. Am. Chem. Soc. **58**, 1486 (1936).
- (11) SÄNGER: Physik. Z. **27**, 556 (1926).
- (12) SMYTH AND MORGAN: J. Am. Chem. Soc. **50**, 1547 (1928).
- (13) SMYTH: Chem. Rev. **6**, 549 (1929).
- (14) SMYTH AND ROGERS: J. Am. Chem. Soc. **52**, 2227 (1930).
- (15) SMYTH AND DORNT: J. Am. Chem. Soc. **53**, 545 (1931).
- (16) SMYTH: Dielectric Constant and Molecular Structure, Chap. 9. The Chemical Catalog Co., Inc., New York (1931).
- (17) SMYTH AND McALPINE: J. Chem. Phys. **2**, 499 (1934).
- (18) SMYTH AND McALPINE: J. Chem. Phys. **3**, 348 (1935).
- (19) SMYTH: Chem. Rev. **19**, 329 (1936).
- (20) VAN ARKEL AND SNOEK: Physik. Z. **33**, 662 (1932); **35**, 187 (1934); Trans. Faraday Soc. **30**, 707 (1934).
- (21) VAN VLECK: J. Chem. Phys. **5**, 556 (1937).
- (22) WYMAN: J. Am. Chem. Soc. **58**, 1482 (1936).

THE PROBLEM OF FREE ROTATION IN COMPLEX DIPOLAR IONS IN SOLUTION¹

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I

We have presented at length elsewhere (14) evidence derived from dielectric constant studies of solutions to show that in simple dipolar ions containing one positive and one negative charge separated by an intervening length of hydrocarbon chain there is nearly complete free rotation about the various single bonds of the chain, and that the ions pass through all the configurations consistent with such free rotation without being stabilized in any preferred configuration. This conclusion applies to the dipolar ions only as they exist in solution in polar liquids, and the argument rests on the view, supported by both empirical and theoretical considerations (11, 12, 13), that in the case of strongly polar liquids the dielectric constant is a linear function of the volume polarization. Granted this, it may be shown from the dielectric constant measurements that the polarization, and consequently the mean square distance between the charges, is proportional to the length of intervening chain, which is exactly what is predicted statistically on the assumption of free rotation and could hardly be expected otherwise. The dipolar ions in point include a very large number of amino acids, peptides, betaines, and other compounds in which the number of atoms in the chain varies from one (e.g., glycine and alanine) to nineteen (glycine heptapeptide).

More recently studies of alicyclic amino acids in which the charged groups of the dipolar ions are attached to the cyclohexane ring have shown that in these molecules also the mean square distances between the charges correspond to the hypothesis of free rotation. So far only four cases of dipolar ions containing more than a single pair of charges have been considered in relation to the question of free rotation (6). These are all straight-chain molecules having the following structures

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- (I) $\text{NH}_3^+(\text{CH}_2)_4 \cdot \text{CH}(\text{COO}^-) \cdot \text{S} \cdot \text{S} \cdot \text{CH}(\text{COO}^-) \cdot (\text{CH}_2)_4 \cdot \text{NH}_3^+$
- (II) $(\text{NH}_2)_2\overset{+}{\text{C}} \cdot \text{NH} \cdot (\text{CH}_2)_4 \cdot \text{CH}(\text{COO}^-) \cdot \text{S} \cdot \text{S} \cdot \text{CH}(\text{COO}^-) \cdot (\text{CH}_2)_4 \cdot \overset{+}{\text{C}} \cdot \text{NH} \cdot (\text{NH}_2)_2$
- (III) $\text{COO}^- \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}(\text{NH}_3^+) \cdot \text{CH}_2 \cdot \text{S} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_3^+) \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{COO}^-$
- (IV) $\text{COO}^- \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}(\text{NH}_3^+) \cdot \text{CH}_2 \cdot \text{S} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_3^+) \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{COO}^-$

All four compounds present a relatively simple case in that each molecule consists of two component dipoles connected by a segment of straight chain involving four single bonds including the S—S linkage. This makes the test for free rotation a particularly simple one. If there is free rotation about all the single bonds the two component dipoles should in each case be oriented very nearly at random with respect to one another, so that the mean square moment of the whole molecule should be the sum of the mean square moments of the two component dipoles, which are known. This turns out to be the case to a very considerable degree of approximation, which shows that in these more complex dipolar ions there is the same degree of free rotation that occurs in the simpler types containing only a single pair of charges.

Unfortunately this simple analysis applicable to the four sulfur compounds cannot in general be used for other types of complex dipolar ions with different charge distributions. Such a case is provided by lysylglutamic acid, a peptide containing two positive and two negative charges, in accordance with the following structure:



Although dielectric constant data are available for this compound (7) no attempt has hitherto been made to analyze them in terms of free rotation. However, the case is not without interest on its own account, and it possesses additional significance because the more general situation in which the molecule cannot be analyzed in terms of two simple component dipoles is almost certain to arise in regard to the proteins and other complex dipolar ions.

In this paper we shall present a more general treatment suitable to such cases, and proceed to apply it to the data for lysylglutamic acid to show that for this dipolar ion also, when it is present in aqueous solution, there is the same evidence for free rotation as for the other dipolar ions which have been studied.

II

The problem which we set ourselves is to reckon the effects of free rotation in complex dipolar ions in a form in which they may be tested for

by dielectric constant measurements of aqueous or strongly polar solutions. Since the dielectric constant is determined by the polarization, our first task is to formulate the effects of free rotation on the mean value of the polarization of the dipolar ions. In these compounds the electric moment is always so large that the contribution of the optical polarization to the total is negligible, and we may with a very high degree of approximation take the total polarization as proportional to the square of the electric moment. Consequently we are led at once to consider the mean square value of the moment for a large number of dipolar ions in which there is free rotation about all the single bonds.

As representing a very general case of a dipolar ion we will consider the model illustrated in figure 1. This consists of a long chain with various side branches at the extremities of which, as well as at the two ends

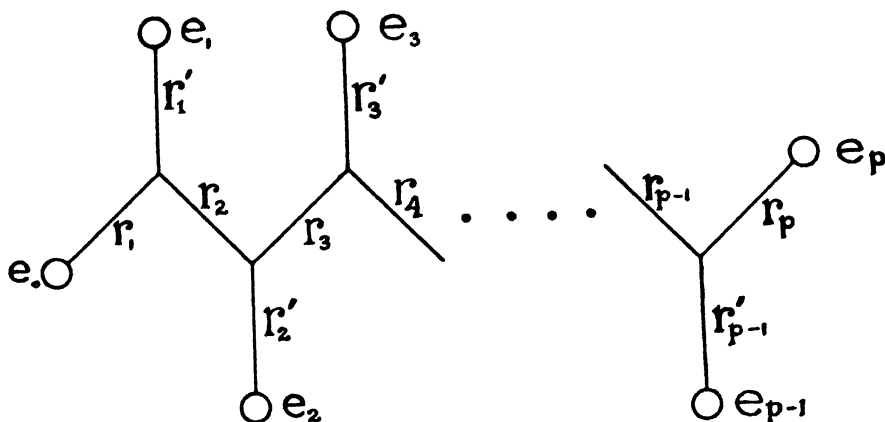


FIG. 1. Model of a dipolar ion

of the main chain itself, are located the charges. The various segments separated by the points of branching will be referred to by the vectors r . We assume that there are p segments in the main chain: r_1, r_2, \dots, r_p ; and $p-1$ branches or side chains: $r'_1 \dots r'_{p-1}$. The number of individual valence bonds or links in the chain segment r_i or r'_i will be denoted by n_i or n'_i . We shall refer to the various charges associated with the different segments by e_0, e_1, \dots, e_p as indicated in figure 1. Each is equal to either plus or minus the elementary charge e .

The energy of the dipolar ion in a homogeneous field of intensity F is given by the scalar product²

$$F \sum_1^p e_i(r_1 + r_2 + \dots + r_i + r'_i) \quad (1)$$

² In this expression we neglect the energy due to the orientation of polar groups of the molecule, e.g., a $\text{CO}\cdot\text{NH}$ group, as well as that due to the optical polarization, in comparison with the energy resulting from the distribution of the ionic charges

We readily see from this that the electric moment of the ion is given by the vector sum Σ . Since $e_i = \pm e$ this sum may also be written as

$$e(a_1 r_1 + \cdots + a_{p-1} r_{p-1} + r_p + r'_1 + \cdots + r'_{p-1}) \quad (2)$$

It is evident from the construction of Σ that the a 's are all whole numbers, the value of each a being determined by the number of positive and negative charges on account of which the corresponding r appears in the sum. An easy rule for computing a , is the following: Replace each e in figure 1 with $+1$ if the charge is positive and with -1 if the charge is negative. Then start at the "right-hand" end of the main chain (i.e., at the position of e_p) and take the algebraic sum of all the values ± 1 associated with the main chain back to and including the value ± 1 corresponding to e_i .

Our task is now to reckon the mean square value of Σ in the form given by equation 2. This quantity involves the mean square values of the various r 's together with the mean values of the various cross terms each consisting of the scalar product of a pair of r 's. We shall now make use of the results of Eyring and Kuhn on free rotation in long-chain molecules to obtain an expression for the mean square values of the r 's and to show that the mean value of each cross term is zero. Eyring (2) calculates that the mean square distance between the ends of a straight-chain molecule consisting of $n+1$ atoms separated by n valence bonds, each of length C_1 , is given by the expression

$$\overline{C^2} = C_1^2 [n + 2(n-1)\cos\theta + 2(n-2)\cos^2\theta + \cdots + 2\cos^{n-1}\theta] \quad (3)$$

in which θ is the supplement of the valence angle. This result presupposes complete free rotation about each valence bond, and is rigorous except for the fact that no account is taken of steric hindrance. It holds for all values of n , even 1 and 2. Kuhn (8), for exactly the same case, obtains the approximate result

$$\overline{C^2} = nC_1^2 \frac{(1 + \cos\theta)}{(1 - \cos\theta)} \quad (4)$$

Both expressions give very nearly the same results for large values of n , but Eyring's expression shows a marked departure from proportionality between $\overline{C^2}$ and n for very small values of n . Thus if we take the valence angle as 110° , equation 3 yields the following values for $\overline{C^2}/nC_1^2$: $n = 2, 1.17$; $n = 3, 1.25$; $n = 4, 1.29$; $n = 10, 1.37$; $n \rightarrow \infty, 1.42$. Kuhn's equation gives 1.42 for all values of n . If n is greater than 3 or 4 the departure from proportionality between $\overline{C^2}$ and n given by equation 3 is probably not much greater than the errors involved in neglecting steric hindrance. Neither equation 3 nor equation 4 can be regarded as strictly applicable to the case of long-chain dipolar ions, since both are derived

for the case of uncharged molecules. More recently Kuhn (9) has given a modified treatment for the case in which each terminal atom of the straight-chain molecule carries a charge, taking account of the Coulomb forces between these charges. For this case, which may be taken as representative of a simple dipolar ion, the values obtained for $\overline{C^2}$ are considerably smaller than those given by the earlier calculations and increase somewhat less rapidly than in proportion to n . The values of $\overline{C^2}$ for small values of n given by this later calculation are almost certainly too small in the light of other evidence (e.g., in regard to glycine), a fact which would tend to emphasize the departure from proportionality in the relation between $\overline{C^2}$ and n . On the whole, therefore, in the light of all the evidence, it would appear that we are justified in writing as an approximate expression for the mean square distance between the two charges in a simple dipolar ion

$$\overline{C^2} = nk \quad (5)$$

in which n is the number of valence bonds in the length of chain between the charges and k is a constant the actual value of which need not concern us. This expression may be expected to hold with a very fair degree of accuracy for values of n greater than 2.

Consider now the vector sum of any two segments r_i and r_j . We may write the mean square value of this sum as follows

$$(r_i + r_j)^2 = r_i^2 + r_j^2 + 2r_i r_j \quad (6)$$

Now assume that the two segments are contiguous and that each contains enough valence bonds so that equation 5 is applicable. Then

$$\overline{r_i r_j} = (n_i + n_j)k - n_i k - n_j k = 0 \quad (7)$$

This result has been derived for the case of two contiguous segments but it applies, *a fortiori*, to the case where r_i and r_j are not contiguous and it is general. A problem arises, however, when one of the segments, e.g., a side chain, consists of only a single link. To be sure, the mean square product of such a segment with any segment not contiguous is zero, but how about its product with a contiguous segment? If the r_j of equation 6 contains only a single valence bond, equation 5 does not apply to it and $\overline{r_i^2}$, which is identical with r_j^2 , is certainly not equal to k . It would seem, therefore, that the conclusion embodied in equation 7 could not hold. Reflection shows, however, that this is not so. Actually we are concerned with r_j only as it forms part of one or more of the greater lengths of chain separating the various charges from one another. Provided only therefore that each of these greater lengths of chain contains enough valence bonds for equation 5 to be applicable to it as a whole, we are justified in

taking $r_j^2 = k$ formally and as a convention for purposes of calculation. No error is introduced, the relation $\overline{r_i r_j} = 0$ becomes applicable to all cases, and a great simplification results.

On the basis of this convention we are now justified in writing as the expression for the mean square value of the moment of the complex dipolar ion:

$$\begin{aligned}\overline{\Sigma^2} &= e^2(a_1^2 r_1^2 + \cdots + a_{p-1}^2 \overline{r_{p-1}^2} + \overline{r_p^2} + \overline{r_1^2} + \cdots + \overline{r_{p-1}^2}) \\ &= e^2 k(a_1^2 n_1 + \cdots + a_{p-1}^2 n_{p-1} + n_p + n_1' + \cdots + n_{p-1}')\end{aligned}\quad (8)$$

The only condition for the applicability of this expression is the one that we have mentioned, namely, that each charge of the dipolar ion should be separated from each other charge by a length of chain containing a sufficient number of valence bonds (i.e., $n > 2$) for equation 5 to be applicable. We see from equation 8 that the mean square value of the moment of the complex dipolar ion is exactly the same as that of a simpler dipolar ion containing only a single pair of charges at the ends of a straight chain for which n is equal to the quantity in parentheses.

The second part of our task is to relate this result to the behavior of the dielectric constant. We shall start with the point of view already mentioned, that in strongly polar liquids such as water and aqueous solutions the dielectric constant is a linear function of the polarization per unit volume; and we shall introduce the concept of the dielectric increment, denoted by δ and defined as the slope dielectric constant-concentration curve, concentration being expressed in moles per liter. We have shown elsewhere (14) that it follows from the linearity of the dielectric constant in terms of the volume polarization that where the molar polarization of solute and solvent do not change with the concentration δ should be independent of concentration, as it is found to be in the case of all the dipolar ions, and that it should be given by

$$\delta = \beta P - \gamma V \quad (9)$$

in which β and γ are constants,³ P is the molar polarization of the solute, and V the volume which it occupies in solution. In the case of dipolar ions, as we have pointed out, P is, to a very high degree of approximation, proportional to the mean square value of the moment. From this it follows by equation 5 that for simple dipolar ions containing a single pair of charges separated by a straight chain consisting of n valence bonds

$$\delta = \beta' n - \gamma V \quad (10)$$

³ β should be independent of the solvent; γ should be characteristic of the solvent.

where γ is the same as in equation 9 but β' is a new constant. So far as data are available δ is found to be linear in n . For the series comprising the aliphatic amino acids it is found that

$$\delta = 13.2n - 3.5 \quad (11)$$

For the series comprising the peptides of glycine

$$\delta = 15n - 7 \quad (12)$$

The volume effect is seen to be small. The fact that the two values 13.2 and 15 are different probably reflects the difference between the C—N and C—C bonds. Both values are presumably slightly less than the true values of β' , since they include the small effects due to the increase of V with n . This, however, presents no problem. Either of the empirical relations 11 and 12 may be used to predict the value of δ corresponding to a given value of n . Now equation 8 tells us how to calculate the value of n for the simple dipolar ion equivalent to any particular complex dipolar ion containing a given number of charges arranged in any given way, subject only to the conditions set forth above. Consequently we have the means of expressing the effects of free rotation in the complex dipolar ion in terms of a dielectric increment.

Let us apply this to the case of lysylglutamic acid. The observed dielectric increment is 345. The value of n for the equivalent simple dipolar ion obtained by applying the rule given above is 22. If we use the empirical relation for the peptides the corresponding dielectric increment is 323. The agreement is to within 6 *per cent*, which is as close as could be expected and would imply that there is the same degree of free rotation in lysylglutamic acid as in the other simpler peptides and amino acids which have been studied.

III

The question arises for lysylglutamic acid, as for other dipolar ions, as to the actual manner in which the free rotation is effective in producing the observed polarizations. The statistical considerations developed above apply to the mean square values of the moments of the dipolar ions in the absence of an external field, and in relating these to the dielectric constant we have proceeded as if each dipolar ion when subjected to a field were oriented as a rigid body without its moment being affected. This treatment of the problem is certainly arbitrary. In view of the flexibility or loose-jointedness resulting from free rotation it would seem likely that each dipolar ion is distorted and assumes a new configuration in the field quite apart from the question of orientation. Kuhn (9) has considered this possibility and concludes that such distortion, at least to a first approximation, should make no difference in the measured polari-

zations. This means that the polarization displayed in a field by a statistically large number of flexible dipolar ions as a result of deformation, without the ions being oriented as units (as if, for instance, one valence bond of each ion were held fixed), is indistinguishable from that displayed as a result of pure orientation without deformation. Reflection shows that Kuhn's conclusion can apply only to the static value of the polarization. Actually there should be a difference between the two kinds of response at frequencies comparable with or greater than those corresponding to the relaxation times of the molecules regarded as rigid bodies. If the dipolar ions contribute to the polarization exclusively by orientation, the dielectric constant should pass through a region of anomalous dispersion at such frequencies; if, on the other hand, they are equally capable of developing a polarization in the alternative manner, then no such region of dispersion should exist. A decision as to which of these alternatives is realized physically must of course ultimately depend on experiment. Unfortunately the relaxation times predictable⁴ for all the dipolar ions other than proteins which have so far been studied are so small that the critical frequencies are greater than or at least of the same order of magnitude as the frequencies used in the measurements. The greater part of the measurements, including all those on the larger peptides, have been made at 10^8 cycles or less, though Devoto in his work has used a frequency about three times this ($\lambda = 90$ cm.). Even for cystinyldidiglycine, with a molecular weight of 504.2, the calculated critical frequency is about 2×10^8 ($\lambda = 1.5$ m.). For smaller dipolar ions the critical frequencies should be smaller, in inverse proportion to the molecular weight. The fact, therefore, that none of the measurements gives evidence of dispersion cannot be regarded as really significant in relation to the problem. It seems *a priori* unlikely that dipolar ions should contribute to the polarization only by orientation as rigid bodies. Certainly in compounds like those represented by formulas I to IV we should expect the two component dipolar ions, connected as they are by a flexible sequence of single bonds, to be able to orient independently of one another, so that the critical frequency should in any case not be less than that corresponding to the relaxation of each half of the molecule regarded as a unit. The case of a structure like lysylglutamic acid is perhaps not so clear.

There are two sets of observations which have an important bearing on the issue. One comprises measurements of the polarizations of various fractions of hydroxydecanoic acid polymers, different fractions being characterized by different mean molecular weights, up to 28,650 (1, 15). These compounds are not dipolar ions, but each consists of a number of polar groups separated by sections of hydrocarbon chain, each section

⁴ By treating the ions as rigid spheres and applying Stokes' formula.

consisting of nine valence bonds about which there is free rotation. They are soluble in benzene, where precise determinations of moments are possible. In this solvent the polarizations of all fractions are the same as those calculated on the basis of free rotation to within 5 per cent or better and are independent of frequency up to 4.8×10^7 ($\gamma = 6.25$ m.), which is almost certainly well above the critical frequency of the larger polymers. These polymers therefore present a clear instance of molecules which, without being oriented as a whole, yet, by virtue of the flexibility due to free rotation about the various valence bonds, exhibit precisely the same polarizations as if they were, with mean square moments equal to those calculated statistically on the assumption of free rotation in the absence of a field.

The other set comprises measurements on proteins in aqueous solution (14, 10, 3). Proteins exist, of course, as dipolar ions, but since the details of their structure remain almost wholly unknown, it is at present impossible to say whether the observed dielectric increments correspond to what would be expected from free rotation or not. The significant fact is that all those proteins which have been studied show the phenomenon of anomalous dispersion at radio frequencies. In the light of what has been said this might be interpreted in either one of two ways. On the one hand we might assume that dipolar ions, at any rate those of the complex type, for some reason behave differently from uncharged polar molecules like the hydroxydecanoic acid polymers: that, although exhibiting statistically the mean square moments calculated for free rotation, they fail to contribute to the polarization except by orientation as rigid bodies. The fact that no dispersion range has been observed for any of the dipolar ions other than the proteins would then be explained on the grounds that the frequencies employed in the measurements have all been too low. On the other hand, we might account for the behavior of the proteins by supposing that they possess an element of rigidity in their structure not found in any of the synthetic peptides which have been studied so far. If so, it would seem, from the work on the cyclohexane amino acids, that this must consist in some structural feature other than the mere formation of alicyclic rings. The latter interpretation is certainly the more plausible, and offers interesting suggestions in regard to protein structure.

SUMMARY

A general procedure has been worked out for calculating the effects of free rotation in complex dipolar ions, containing a given number of charges arranged in any given way, in terms of a dielectric increment for an aqueous solution. The procedure has been applied to the case of lysyl-glutamic acid, which, like other dipolar ions previously considered, is

found to meet the test of free rotation. Possible implications of these results in terms of protein structure have been discussed.

REFERENCES

- (1) BRIDGMAN, W. B., AND WILLIAMS, J. W.: J. Am. Chem. Soc. **59**, 1579 (1937).
- (2) EYRING, H.: Phys. Rev. [2]**39**, 746 (1932).
- (3) FERRY, J. D., AND ONCLEY, J. L.: J. Am. Chem. Soc. **60**, 1123 (1938).
- (4) GREENSTEIN, J. P., AND WYMAN, J., JR.: J. Am. Chem. Soc. **57**, 637 (1935).
- (5) GREENSTEIN, J. P., AND WYMAN, J., JR.: J. Am. Chem. Soc., in press.
- (6) GREENSTEIN, J. P., AND WYMAN, J., JR.: J. Biol. Chem., in press.
- (7) GREENSTEIN, J. P., WYMAN, J., JR. AND COHN, E. J.: J. Am. Chem. Soc. **57**, 637 (1935).
- (8) KUHN, W.: Kolloid Z. **68**, 2 (1934).
- (9) KUHN, W.: Z. physik. Chem. **A175**, 1 (1935).
- (10) ONCLEY, J. L.: J. Am. Chem. Soc. **60**, 1115 (1938).
- (11) ONSAGER, L.: J. Am. Chem. Soc. **58**, 1486 (1936).
- (12) VAN VLECK, J. H.: J. Chem. Phys. **5**, 556 (1937).
- (13) WYMAN, J., JR.: J. Am. Chem. Soc. **58**, 1482 (1936).
- (14) WYMAN, J., JR.: Chem. Rev. **19**, 213 (1936).
- (15) WYMAN, J., JR.: J. Am. Chem. Soc. **60**, 328 (1938).

THE APPARENT AND PARTIAL MOLAL HEAT CAPACITIES AND VOLUMES OF GLYCINE AND GLYCOLAMIDE¹

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Within the last decade the Debye-Hückel theory has been extended to explain fairly satisfactorily the behavior of dilute electrolytic solutions. The change of the logarithm of the activity coefficient, the apparent (or partial) molal heat content, heat capacity, volume, compressibility, and expansibility has been shown, theoretically and experimentally, to be a linear function of the square root of the volume concentration, c . The rate of change of all these properties with the square root of the concentration depends upon the valence type of the salt and increases as the ions carry larger charges. These results have been discussed in a number of review articles (14, 24, 15) and books (23, 11).

In general, non-electrolytes behave more like perfect solutes than do electrolytes, but they also show appreciable deviations, when studied carefully. Theoretical work by Fuoss (12) has indicated that many of these deviations may be due to the mutual interaction of dipolar solute molecules. The limiting slopes of the thermodynamic properties of such solutions should be linear functions of the *first power* of the concentration, and should increase with increasing dipole moment. As E. Q. Adams (1) and Bjerrum (2) showed a number of years ago, amino acids in aqueous solutions exist almost wholly as zwitter ions, with large dipole moments which Wyman (30) has evaluated from the large increase in the dielectric constant of their aqueous solutions. Cohn and his collaborators³ have studied many properties of the amino acids in solution. With the help of theoretical investigations by Scatchard (28) and Kirkwood (22) they have correlated these properties with the zwitter-ionic nature of the solutes in a most illuminating way. A stimulating review, entitled "The Chemistry of the Proteins and Amino Acids," was published by Cohn three years ago (4).

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² The first and second authors measured the specific heats; the second author measured most of the densities; the third author measured the densities of the dilute solutions and of solid glycolamide.

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Our work developed from calculations of the heat capacities of zwitter ions made by Edsall (9) and from a discussion with Professor Cohn, who very kindly offered to furnish the necessary purified material. We are planning a systematic study of the heat capacities and heats of dilution of solutions of the amino acids and their uncharged isomers and of the densities of those solutions for which values are not now known accurately. Such a study should show clearly the effect of the charged groups on the thermodynamic behavior of the solutes. The present article deals with the apparent molal heat capacities and volumes of glycine, $^+\text{H}_3\text{NCH}_2\cdot\text{COO}^-$, and of its uncharged isomer, glycolamide, $\text{CH}_2\text{OH}\cdot\text{CONH}_2$.

MATERIALS AND SOLUTIONS

Most of the glycine used in this investigation was very kindly purified for us by Dr. John T. Edsall.⁴ The original material, prepared by the Dow Chemical Company, was recrystallized four times from hot water. Dr. Edsall reported that Kjeldahl analyses gave 18.71 and 18.74 per cent nitrogen, which agreed within experimental error with the theoretical value of 18.66 per cent. His conductivity measurements indicated about 0.01 per cent of electrolytic impurity (calculated as ammonium chloride), which would have no appreciable effect upon our specific heat measurements.

The material furnished by Dr. Edsall was supplemented by a second lot, which Mr. Keko prepared in this laboratory by the method of Orten and Hill (26). This material gave no test for ammonia with Nessler's reagent or for chloride with silver nitrate. A 0.9 *m* solution (experiment 9) showed a small amount of insoluble residue, but its specific heat was only 0.017 per cent lower than that calculated from our other results. Filtration and one further crystallization gave a product which dissolved completely. Conductance measurement showed a salt content of 0.01 per cent (as ammonium chloride). This material was identical in the specific heats and densities of its solutions with the material supplied by Dr. Edsall.

The first sample of glycolamide was furnished by Dr. Edsall. It was made by passing dry ammonia gas into a solution of ethyl glycolate dissolved in well-dried absolute alcohol. When the solution was saturated it was allowed to stand for several days, and was then evaporated to dryness under reduced pressure. The glycolamide was recrystallized thrice from hot ethanol. Dr. Edsall reported that it gave no test for ammonia with Nessler's reagent, and showed 18.54 and 18.60 per cent amide nitrogen, which agrees within experimental error with the theoretical value (18.66 per cent). The uncorrected melting point of 118°C. is slightly lower than some reported in the literature.

⁴ Of the Department of Physical Chemistry of the Harvard Medical School.

Since the solubility of glycolamide in water is about twice as great as that of glycine, we were unable to cover the whole range of concentration with the material at our disposal. We therefore prepared a second lot, and we are now engaged in determining the specific heats and densities of the concentrated solutions. These results are not necessary for the purposes of our present comparison but will be published subsequently.

Because of the limited amount of material at our disposal, we reclaimed it from each solution after use. The glycine solutions were evaporated to saturation under reduced pressure at about 40°C. Three volumes of ethanol were then added and the solution chilled with ice. This precipitated all but about 1.6 per cent of the glycine (7) as small crystals which were filtered on a platinum sponge crucible and dried *in vacuo*. The ethanol was purified by refluxing for 3 to 4 hr. with sulfuric acid and distilling from a good column. This treatment was found by Leighton (25) to yield very pure alcohol.

The glycolamide was reclaimed by evaporating to dryness at 35–40°C. under reduced pressure; it was then dissolved in pure hot ethanol and crystallized at 0°C. The crystals were collected on a platinum filter and dried *in vacuo*.

Solutions of glycine and glycolamide must be protected from contamination with microorganisms. Some of our glycine solutions which had stood for a week developed small thread-like pieces of white mold. Professor Edgecombe⁵ very kindly prepared a culture of this material and sent it to the Bureau of Plant Industry of the United States Department of Agriculture, where it was identified as a species of *Fusarium*. At Professor Edgecombe's suggestion, we filtered the solutions through a sterilized Mandler filter of diatomaceous earth to remove the mold and spores. By sterilizing all apparatus with heat at frequent intervals, filtering or boiling all the distilled water, and using solutions immediately, we were able to prevent appreciable contamination. Whenever a thread or two of mold appeared, the solution was put through a bacterial filter before reclaiming the material in it.

The distilled water used in making up the solutions had a specific conductance of less than 2×10^{-6} mhos. It was deaerated immediately before use. Most of the solutions were made up determinate from this water and the solid, which was dried *in vacuo* at 40°C. in the same manner as the organic materials used in previous work in this laboratory (16, 17). Three glycine solutions were made by quantitative dilution with water. The weights were calibrated and all weighings were reduced to the vacuum standard, using the value 1.607 for the density of glycine (7) and 1.390 for that of glycolamide, determined in this investigation.

The density of each solution was used as a check on its concentration.

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The first four glycine solutions were made in a volumetric flask, calibrated to deliver the correct volume to the calorimeter at 25°C. Their densities were calculated to about 0.1 per cent. In the other experiments an extra amount of solution was made and its density was determined to ± 0.1 per cent, usually in duplicate, in 10-ml. pycnometers. The densities of the glycine solutions were compared with a large-scale plot of the consistent results of Dalton and Schmidt (8) and of Cohn and his collaborators (3, 5) covering the whole range of concentration. Our values agreed with these within experimental error in nearly every case. Where discrepancies occurred, we concluded that they indicated an error in making our solution and discarded the results, as explained in the next section.

No densities of glycolamide solutions were found in the literature, but the correctness of our concentrations was indicated by the self-consistency of the densities we determined.

SPECIFIC HEATS AND APPARENT MOLAL HEAT CAPACITIES

The experimental results

The specific heats were measured with the differential apparatus, employing variable heaters, that has been developed in this laboratory (18) and has been found to give results reproducible on the average to 0.01 per cent or better. Table 1 contains the results for the glycine solutions, numbered chronologically. Those lettered a and b were made by quantitative dilution of portions of the original solution. Experiment 2 (2.85 *M*) was discarded because the solution deposited solid glycine in the calorimeter when it stood overnight a few degrees below 25°C. Experiments 3a and 4 were discarded because of discrepancies in the densities, which cast doubt upon the concentrations of the solutions. Experiment 9 was discarded because of a trace of insoluble matter, and experiment 10 when an error was found in the amount of solution weighed into the calorimeter. Table 1 contains all the results for glycine except those affected by the known errors explained above. Table 2 contains the results of all the experiments with glycolamide.

In these tables the molality, *m*, was calculated directly from the weights of the constituents, using for the molecular weight of glycine and glycolamide the value $M_2 = 75.0685$ (1938 atomic weights). The molarity, *c*, was calculated from the weights and the densities in all the experiments except the first four with glycine, where it was calculated from the weight of glycine and the volume of the flask. The specific heat is relative to water at the same temperature. The apparent molal heat capacity is calculated from the usual equation

$$\Phi C_{p_2} = \left[\frac{1000}{m} + M_2 \right] s - \frac{1000}{m} \quad (4)$$

TABLE 1*

Specific heats and apparent molal heat capacities of glycine at 5°, 25°, and 40°C.

EXPT. NO.	c AT 25°C.	m	5°C.			25°C.			40°C.		
			s	$10^3 \Delta s$	ΦC_{p_2}	s	$10^3 \Delta s$	ΦC_{p_2}	s	$10^3 \Delta s$	ΦC_{p_2}
	0.0000	0.0000	1.00000			1.00000			1.00000		
1b	0.0983	0.0990				0.99353†	0	9.3			
10	0.1002	0.1009	0.99211†	-4	-3.8				0.99387	-3	13.8
3b	0.1995	0.2019				0.98699†	0	9.7			
1a	0.2989	0.3042				0.98074†	2	10.3			
12	0.2997	0.3055	0.97713†	5	-1.50	0.98061	0	10.2	0.98201†	4	14.8
1	0.3995	0.4078				0.97446†	-4	10.6			
8	0.6010	0.6190	0.95604	-2	0.76	0.96241	2	11.52	0.96487	1	15.68
11	0.8918	0.9311	0.93727	-2	2.99	0.94566	-5	12.63	0.94901	-5	16.48
7	1.2001	1.2710	0.91886	1	5.14	0.92905	3	13.92	0.93315	2	17.46
6	1.7991	1.9629	0.88624†	0	8.57	0.89899	2	16.02	0.90421	-2	19.07
5	2.3976	2.6972				0.87151	7	17.79	0.87767	3	20.53
3	2.695	3.0792				0.85844†	-3	18.47			
Average.				±2			±3			±3	

* In tables 1 and 2 experiments are numbered chronologically. c (at 25°C.) is the molarity (moles of solute per liter of solution at 25°C.), and m is the molality (moles of solute per 1000 g. of water). Δs is the difference between the observed specific heat, s , and that calculated from the equation for the apparent molal heat capacity, ΦC_{p_2} , listed in table 3.

† These results are the average of two pairs of experiments instead of one.

TABLE 2

Specific heats and apparent molal heat capacities of glycolamide at 5°, 25°, and 40°C.

EXPT. NO.	c AT 25°C.	m	5°C.			25°C.			40°C.		
			s	$10^3 \Delta s$	ΦC_{p_2}	s	$10^3 \Delta s$	ΦC_{p_2}	s	$10^3 \Delta s$	ΦC_{p_2}
	0.0000	0.0000	1.0000			1.00000			1.00000		
2	0.1985	0.2014	0.99047	2	27.1	0.99223	0	35.9	0.99297	2	39.7
6	0.4002	0.4107	0.98099	-4	27.4	0.98444	0	36.0	0.98588	8	39.7
5	0.7547	0.7905	0.96512	1	28.33	0.97109	6	36.33	0.97332	-10	39.31
4	1.1985	1.2890	0.94619	1	29.29	0.95467	-7	36.50	0.95808	-4	39.40
3	1.5994	1.7632	0.92999	0	30.11	0.94048	-2	36.84	0.94475	11	39.59
1	2.3019	2.6537	0.90342	2	31.42	0.91666	0	37.41	0.92229	-2	39.95
Average.				±2			±3			±6	

It is therefore expressed in caloric units at the temperature of the experiment.

The values of the apparent molal heat capacities were found to lie along smooth curves, linear in the dilute region, when they were plotted

against either the molality or the molarity. The slope and curvature were greater in the case of glycine. Using the molality as abscissa for convenience in calculation, a power series of the type

$$\Phi C_{p_2} = \Phi^0 C_{p_2} + am + bm^2 \quad (5)$$

proved adequate to reproduce the results over the whole range of concentration. The coefficients, given in table 3, were determined at each temperature by the method of least squares, weighting each value of the apparent molal heat capacity according to its probable accuracy, measured by the reciprocal of $[1000/m + M_2]$. In the specific heats the average deviation of the experimental points from the lines represented by these equations was ± 0.003 per cent. The excellent agreement is shown by

TABLE 3

Equations for the apparent molal heat capacities of glycine and glycolamide and the partial molal heat capacities of solute and solvent at 5°, 25°, and 40°C.

		GLYCINE	GLYCOLAMIDE
At 5°C.	$\Phi C_{p_2} =$	$-4.30 + 9.01m - 1.25m^2$	$26.55 + 2.39m - 0.21m^2$
	$\bar{C}_{p_2} =$	$-4.30 + 18.02m - 3.75m^2$	$26.55 + 4.78m - 0.63m^2$
	$\bar{C}_{p_1}^0 - \bar{C}_{p_1} =$	$0.1623m^2 - 0.0450m^3$	$0.0431m^2 - 0.0076m^3$
At 25°C.	$\Phi C_{p_2} =$	$8.83 + 4.58m - 0.47m^2$	$35.76 + 0.62m$
	$\bar{C}_{p_2} =$	$8.83 + 9.16m - 1.41m^2$	$35.76 + 1.24m$
	$\bar{C}_{p_1}^0 - \bar{C}_{p_1} =$	$0.0825m^2 - 0.0169m^3$	$0.0112m^2$
At 40°C.	$\Phi C_{p_2} =$	$13.74 + 3.27m - 0.28m^2$	$39.72 - 0.52m + 0.28m^2$
	$\bar{C}_{p_2} =$	$13.74 + 6.54m - 0.84m^2$	$39.72 - 1.04m + 0.69m^2$
	$\bar{C}_{p_1}^0 - \bar{C}_{p_1} =$	$0.0589m^2 - 0.0101m^3$	$-0.0094m^2 + 0.0083m^3$

the plots of the results made in figure 1. The curves will be discussed in more detail in a later section.

Comparison with other investigations

No studies of the specific heats of glycolamide solutions could be found, but glycine solutions have been studied by Zittle and Schmidt (32). They used twin Dewar flasks, one of which supplied a reference temperature, while the solution in the other was heated through a measured temperature interval. They tabulated values of the specific heat and partial and apparent molal heat capacities at even concentrations, read from a smoothed plot of their original data, and concluded that the apparent and partial molal heat capacities were linear functions of the molality. The average difference between their tabulated specific heats and those calculated from our equation is ± 0.6 per cent, while the maximum, in the nearly saturated solution, is 0.9 per cent. In this comparison we took into ac-

count their use of the 15°- instead of the 25°-caloric. In order to make a more satisfactory check of this work, we turned to the original data of Zittle (31) and plotted the fifty specific heats against the molality on a large scale. A comparison with the smooth curve through our experimental results showed an average deviation of ± 0.5 per cent, which is the same as the average difference between his duplicate experiments. Up to 1.2 *m* his results are equally distributed above and below our curve, with an average deviation of ± 0.4 per cent, and therefore agree nicely with ours. At the higher concentrations his results all fall *below* our curve,

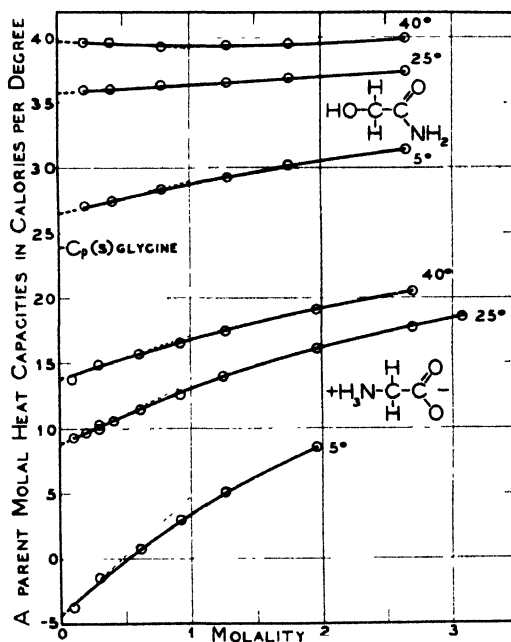


FIG. 1. Apparent molal heat capacities of glycine and glycolamide at 5°, 25°, and 40°C.

with an average deviation of 0.85 per cent. This is so near his own experimental uncertainty that the difference probably is not significant.

Partial molal heat capacities

The partial molal heat capacities of solute and solvent are easily calculated from the coefficients of equation 5 by means of the equations used in a previous article from this laboratory (16).

$$\bar{C}_{p_2} = \Phi^0 C_{p_2} + 2am + 3bm^2 \quad (6)$$

$$\bar{C}_{p_1} - \bar{C}_{p_1}^0 = 10^3 M_1 (am^2 + 2bm^3) \quad (7)$$

where M_1 is the molecular weight of water, 18.016, and \bar{C}_{p1}^0 is the molecular heat capacity of pure water, which has the same numerical value, since the unit is the calorie per degree at the experimental temperature. The numerical coefficients of these equations are collected in table 3.

DENSITIES AND APPARENT MOLAL VOLUMES

The densities of aqueous solutions of glycine have been studied by Dalton and Schmidt (8) and by Cohn and his collaborators (3, 5, 7) at 25°C. from the saturated solution (2.9 M) to the 0.16 M solution. Cohn (5) found that the apparent molal volume of glycine was a linear function of the molarity, c , from 2.5 to 0.25 moles per liter. Our determinations of the densities of the solutions used for specific heat measurements confirmed these findings. In order to extend these measurements to low concentrations, we made a very careful determination of the densities of four dilute solutions, using 60-ml. pycnometers differentially, as described in a recent article from this laboratory (19). All of our results are presented in table 4.

The apparent molal volumes were calculated from the usual equation

$$\Phi V_2 = \frac{1000}{c} \left[\frac{d_1 - d}{d_1} \right] + \frac{M_2}{d_1} \quad (8)$$

where d_1 and d are the densities of water and solution and the other symbols have their previous significance. A plot of the apparent molal volumes from our work and from that of the previous investigators is shown in figure 2. The solid line corresponds to the equation listed in table 6. The coefficients were calculated from our results and those of Cohn and his collaborators by the method of least squares, weighting each result by the factor $p(d_1 - d)$, where p was estimated from the self-consistency of the series. It was assigned the value 1 for our experiments at higher concentrations, 4 for those of Cohn and his collaborators, and 50 for our results at low concentrations. The agreement between the points and the line is excellent, averaging ± 0.0006 per cent in the density for our low concentration experiments, ± 0.014 per cent for those at high concentration, and ± 0.005 per cent for those of Cohn. The only serious discrepancy was in the density of the saturated solution given by Cohn, McMeekin, Edsall, and Weare (7), which is 0.08 per cent lower than that calculated from our line. This value undoubtedly would be subject to the greatest experimental uncertainty, and was not considered in our calculations. The results of Dalton and Schmidt agree with our line, on the average, within ± 0.013 per cent in the density. They are consistently higher in the less concentrated solutions and lower in the more concentrated ones, but the maximum deviation is 0.04 per cent.

Since we could not find the density of solid glycolamide in the literature, we determined it in a specific gravity bottle of the usual design, having a

ground-glass stopper with a capillary opening. We found that the amide was not appreciably soluble in *n*-heptane, which was used as confining liquid. The bottle was calibrated with water at 25°C. and gave a value

TABLE 4*

Densities of aqueous solutions of glycine at 25°C. and corresponding apparent and partial molal volumes

EXPT. NO.	<i>c</i>	<i>m</i>	<i>d</i>	Δd (IN P.P.M.)	ΦV_2 (OBSERVED)	\bar{V}_2 (CALCULATED)	\bar{V}_1 (CALCULATED)
	0.00000	0.00000	0.997074			43.199	18.0691
6a	0.1002	0.1009	1.00026	-10	43.4	43.38	18.0689
b			1.00011	-160	44.9		
11a	0.10056	0.10129	1.000287	4	43.24	43.38	18.0689
b			1.000285	2	43.26		
9a	0.20112	0.20348	1.003489	15	43.30	43.54	18.0685
b			1.003484	10	43.32		
8a	0.40024	0.40853	1.009749	7	43.53	43.88	18.0666
b			1.009744	2	43.54		
10a	0.59794	0.61579	1.015898	-1	43.72	44.21	18.0635
b			1.015898	-1	43.72		
4a	0.6010	0.6190	1.01598	80	43.73	44.22	18.0635
b			1.01582	-80	44.00		
7a	0.8918	0.9311	1.02481	-120	44.09	44.71	18.0567
b			1.02471	-220	44.21		
5a	1.0003	1.0496	1.02821	-10	44.07	44.88	18.0535
b			1.02800	-220	44.28		
3a	1.2001	1.2701	1.03414	-110	44.31	45.21	18.0467
b			1.03453	290	43.98		
2a	1.7991	1.9629	1.05167	-190	44.85	46.17	18.0189
b			1.05160	-260	44.95		
1a	2.3976	2.6972	1.06880	-50	45.28	47.09	17.9801
b			1.06900	150	45.20		

* In tables 4 and 5 the experiments are numbered chronologically. *c* and *m* represent the molarity and molality, respectively, as in tables 1 and 2; *d*, the density of the solution in grams per milliliter; and Δd , the observed density minus that calculated from the linear equation in table 6. The density of pure water is taken from the International Critical Tables, Vol. III, p. 25. The densities in experiments 8 to 11 were determined in 60-ml. pycnometers, the others in 10-ml. ones.

for the density of *n*-heptane within 0.01 per cent of that given in the International Critical Tables (21). Two separate experiments gave the density of the amide as 1.3890 and 1.3905, averaging 1.390 g. per milliliter.

Recently we have learned from Dr. Edsall of an unpublished determination of the density of solid glycolamide, made by Dr. T. L. McMeekin.⁴ Using benzene as the confining liquid, he obtained a value 0.8 per cent higher than ours.

The densities of the amide solutions were determined like those of the glycine solutions, the 60-ml. pycnometers being used only for nine of the most dilute solutions. The results are presented in table 5. The corre-

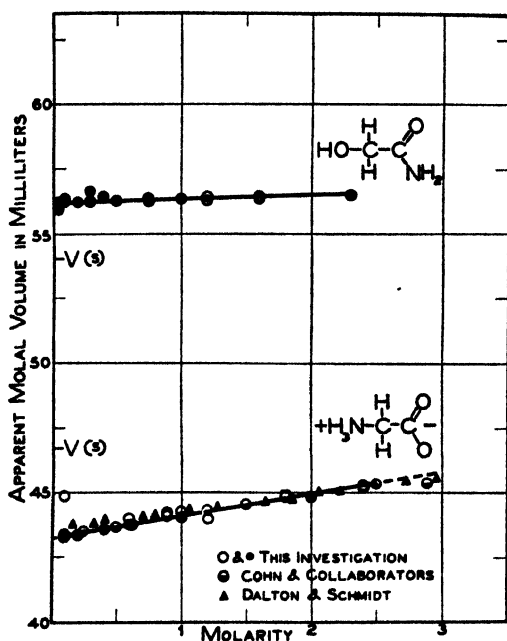


FIG. 2. Apparent molal volumes of glycine and glycolamide at 25°C.

sponding values of the apparent molal volume, plotted in figure 2, were found to lie along a straight, nearly horizontal line, represented by the equation listed in table 6. The coefficients were determined as before by the method of least squares, omitting experiment 11. The agreement between the other points and the line was very satisfactory, averaging ± 0.0007 per cent in the density for the results with the 60-ml. pycnometers and ± 0.005 per cent for the others. Experiment 11 differed by ten times the average amount.

Dr. Edsall has called our attention to an unpublished determination of the density of a 0.2704 molar solution of glycolamide at 25°C., also made

TABLE 5*
Densities of aqueous solutions of glycolamide at 25°C. and corresponding apparent and partial molal volumes

EXPT. NO.	c	m	d	Δd (IN P.P.M.)	ΦV_2 (OBSERVED)	V_2 (CALCULATED)	V_1 (CALCULATED)
	0.00000	0.00000	0.997074			56.156	18.0691
10a	0.04992	0.05021	0.998042	16	55.84	56.17	18.0691
b			0.998035	9	55.98		
15a	0.04993	0.05022	0.998027	1	56.15	56.17	18.0691
b			0.998023	-3	56.23		
8a	0.09985	0.10071	0.998968	-10	56.26	56.19	18.0690
b			0.998964	-14	56.30		
13a	0.10038	0.10125	0.998990	3	56.15	56.19	18.0690
b			0.998986	-1	56.19		
9a	0.19695	0.19974	1.000829	4	56.17	56.22	18.0690
b			1.000823	-2	56.20		
2a	0.1985	0.2014	1.00086	5	56.2	56.22	18.0690
b			1.00083	-25	56.2		
12a	0.30127	0.30736	1.002807	0	56.20	56.25	18.0688
b			1.002806	-1	56.21		
11a†	0.30635	0.31267	1.002786	-117	56.59		
b			1.002779	-124	56.61		
6a	0.4002	0.4107	1.00462	-113	56.4	56.28	18.0686
b			1.00473	-3	56.4		
7a	0.51506	0.53198	1.006863	5	56.23	56.32	18.0683
b			1.006856	-2	56.24		
5a	0.7547	0.7905	1.01138	0	56.27	56.40	18.0675
b			1.01132	-60	56.33		
14a	1.00049	1.06335	1.015973	-28	56.34	56.47	18.0662
b			1.015991	-10	56.33		
4a	1.1985	1.2890	1.01977	61	56.29	56.53	18.0650
b			1.01963	-79	56.41		
3a	1.5994	1.7632	1.02725	72	56.38	56.64	18.0617
b			1.02712	-58	56.45		
1a	2.3019	2.6537	1.04022	77	56.49	56.84	18.0538
b			1.04017	27	56.51		

* The densities in experiments 7 to 15 were determined in 60-ml. pycnometers, the others in 10-ml. ones.

† The value of Δd in experiment 11 is more than ten times as large as the average value of Δd for all other experiments with 60-ml. pycnometers. This large discrepancy is shown in figure 2. This determination was omitted from the calculation of the equations for density and apparent molal volume.

by Dr. McMeekin. He found a molal volume of 56.21 ml., which agrees excellently with the value of 56.20 ml. calculated from our equation. Dr. McMeekin apparently was the first person to suggest and make a comparison of the properties of amino acids and those of their uncharged isomers.

The equations for the apparent molal volumes of glycine and glycolamide were used to calculate the density as a function of the molarity and also to calculate the partial molal volumes of solute and solvent, as in the recent paper from this laboratory to which we referred before (19). The differences between the observed and calculated densities are listed in tables 4 and 5, as are also the values of \bar{V}_2 and \bar{V}_1 . The corresponding equations are given in table 6.

TABLE 6

Equations for the densities and apparent molal volumes of glycine and glycolamide and the partial molal volumes of solute and solvent at 25°C.

	GLYCINE	GLYCOLAMIDE
$d =$	$0.997074 + 0.031996c - 8.589 \times 10^{-4}c^2$	$0.997074 + 0.019076c - 1.590 \times 10^{-4}c^2$
$\Phi V_2 =$	$43.199 + 0.8614c$	$56.156 + 0.1595c$
$\bar{V}_2 =$	$43.199 + \left[\frac{2000 - 43.199c}{1000 + 0.8614c^2} \right] 0.8614c$	$56.156 + \left[\frac{2000 - 56.156c}{1000 + 0.1595c^2} \right] 0.1595c$
$\bar{V}_1 =$	$\frac{18069.1}{1000 + 0.8614c^2}$	$\frac{18069.1}{1000 + 0.1595c^2}$

DISCUSSION OF RESULTS

The similarity between the apparent molal volume and heat capacity curves is at once apparent from figures 1 and 2. In each case the curve for glycine is lower than that for the amide and the curvature is much greater. The small value of the apparent molal volume of glycine has been discussed by Cohn, McMeeken, Edsall, and Blanchard (6) in an article dealing with the apparent molal volume of amino acids and the electrostriction of the solvent. In this connection it is interesting to compare the molal volumes of solid glycolamide, 54.01 ml., and of solid glycine, 46.71 ml. (7). The difference of 7.30 ml. shows the much closer packing in the crystal lattice of glycine, due to the electrostatic forces. In an infinitely dilute solution the apparent (or partial) molal volume of glycolamide is 56.16, 2.15 ml. *larger* than that of the solid. If we take Gibson's (13) value of 10 per cent as the normal increase in volume on melting, we would estimate an apparent molal volume of 59.4 ml. for glycolamide if it formed a perfect solution. The difference, due to electrostriction, amounts to only about 3.2 ml. In the case of the glycine, how-

ever, the limiting value of the partial molal volume is 3.51 ml. *less* than the molal volume of the solid, showing that the electrostrictive effect upon the solvent is even greater than that in the crystal lattice. The difference of 12.96 ml. between the apparent molal volumes of glycine and of glycolamide in the infinitely dilute solution is probably the best available figure for the difference due to the zwitter ion in solution. This value is very near the 13.3 ml. which Cohn (6) deduced as the average difference between the apparent molal volumes calculated for solid uncharged amino acids and those found for the zwitter ions in 0.25 *m* solution at 25°C. In comparison with the hypothetical uncharged liquid, the total electrostriction in solution would amount to about 16.2 ml.

In the case of glycine the molal heat capacity of the solid at 25°C. is 23.9 cal. per degree, according to Parks (27). The apparent molal heat capacity at infinite dilution is 15.2 cal. per degree less at 25°C. This difference varies enormously with temperature, being twice as great at 5°C. and only two-thirds as large at 40°C. The heat capacity of solid glycolamide could not be found in the literature.

In comparing the apparent molal heat capacity curves, the lower value for glycine would be expected on general grounds. The decrease in heat capacity caused by the formation of free ions is well known and amounts to 50.6 cal. per degree per mole in the case of water and its ions (14). The decrease in the formation of ammonium and acetate ions from undissociated ammonia and acetic acid was estimated by Edsall (9) from thermochemical and E.M.F. data as 43 to 47 cal. per degree per mole. He predicted that the corresponding formation of a zwitter ion from the uncharged α -amino acid would cause a somewhat smaller decrease, because the resulting charges were too close to exert their maximum electrostriction upon the water. Recently he sent us the results of some interesting calculations which have not been published elsewhere and which we are presenting here with his permission (10).

Taking the change of the second dissociation constant of several amino acids from the recent data of Smith (29), Edsall finds for the reaction:



$$\Delta C_{p_1} = -7 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (5^\circ\text{C.})$$

$$\Delta C_{p_1} = +25 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (40^\circ\text{C.})$$

This reaction can be represented as the sum of two others:



and



Assuming that the change of heat capacity in the last reaction is about the same as that for the ionization of acetic or propionic acid, he took the results of Harned and Ehlers (20) for propionic acid and found:

$$\Delta C_{p_1} = 35 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (5^\circ\text{C.})$$

$$\Delta C_{p_1} = 39 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (40^\circ\text{C.})$$

By subtraction he obtained for the change from uncharged acid to zwitter ion:

$$\Delta C_{p_2} = -35 - 7 = -42 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (5^\circ\text{C.})$$

$$\Delta C_{p_2} = -39 + 25 = -14 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (40^\circ\text{C.})$$

Although these calculations involve the usual uncertainties inherent in the second derivatives of E.M.F. data, they suggested that we might find a much greater difference between glycine and glycolamide at low than at high temperatures. We therefore made the series of measurements at 5°C. and 40°C. The results show a decrease in $\bar{C}_{p_2}^0$ of 31.3, 26.9, and 25.5 calorie units at 5° , 25° , and 40°C. The decrease is smaller at the higher temperatures, as Edsall's calculations predicted, but the change with temperature is much smaller than the E.M.F. data indicate. Qualitatively, the difference due to the zwitter-ionic structure of the α -amino acid is about as much less than that due to complete ionization as we would expect.

Although we can correlate most of these results qualitatively with the effect of electrostriction upon the volume and heat capacity of the solvent, we have as yet no theory which will predict quantitatively the behavior of aqueous solutions of dipolar solutes like the amino acids. Kirkwood (22) has dealt with the effect of ions upon the activity and solubility of amino acids, and Fuoss (12) has made an attack upon the theory of dipole-dipole interaction which would be necessary to calculate the change of apparent molal volume and heat capacity with concentration. He has obtained an expression for the contribution of the dipole moment to the free energy in terms of the parameter:

$$x = \mu^2/a^3DkT$$

where μ is the dipole moment, a is the atomic radius, D is the dielectric constant of the medium, k is Boltzmann's constant, and T is the absolute temperature. He has reduced the general integral equation to a solution in two special cases: when x is very *large* (ionic pairs in a solvent of low dielectric constant) and when x is very *small*. Unfortunately, in the case of glycine x is about 2, and hence neither special case will fit. He has shown that, at least in the case where x is very small, the apparent molal heat capacity should be a linear function of the concentration, and that

its slope should be greater for the higher dipole moment, as we have found experimentally at low concentrations. A similar result can also be shown to follow for the apparent molal volume. His equation for the heat capacity, however, lacks the factor involving first and second temperature derivatives of the dielectric constant of the solvent which must enter in. Since the theoretical slope of the heat of dilution curve involves only the first derivative and is much less complicated, we hope to be able to develop the theory to a point where it can be compared with our studies of heats of dilution.

SUMMARY

We have measured the specific heats of aqueous solutions of glycine and of glycolamide at 5°, 25°, and 40°C., over a range of concentration from 0.1 or 0.2 molal to the nearly saturated solution. We have calculated the apparent molal heat capacity of these solutes, and find that it is approximately a linear function of the molality. The value at infinite dilution is about 27 cal. per degree per mole less for glycine than for glycolamide, and the slope is appreciably greater.

We have measured the density of aqueous solutions of the same solutes at 25°C., from 0.1 molal concentration to the nearly saturated solution, and find the apparent molal volume is a linear function of the molarity over this range. The limiting value of the apparent molal volume of glycine is 12.96 ml. less than that of the uncharged isomer, and this may be taken as the value of the electrostriction of the solvent. The slope of the glycine curve is very much steeper than that of glycolamide.

These observed differences are discussed in terms of the electrostriction and mutual interaction of the zwitter ions.

The partial molal volumes and heat capacities of glycine and of glycolamide are calculated as functions of the concentration and are presented in tabular form.

It is a pleasure to acknowledge our indebtedness to Professor Cohn and Dr. Edsall for most of the materials used in this work; to Mr. Keko who, working on an N.Y.A. grant, prepared some of the glycine; to Professor Edgecombe for his advice and assistance in controlling the contamination of our solutions; and to the Graduate School of Northwestern University for a Research Grant to the senior author, which financed part of the assistance in this work.

REFERENCES

- (1) ADAMS, E. Q.: *J. Am. Chem. Soc.* **38**, 1503 (1916).
- (2) BJERRUM: *Z. physik. Chem.* **104**, 147 (1923).
- (3) BRIDGMAN, P. W., AND DOW: *J. Chem. Phys.* **3**, 35 (1935).
- (4) COHN, E. J.: *Ann. Rev. Biochem.* **4**, 93 (1935).

- (5) COHN, E. J., AND DANIEL: J. Am. Chem. Soc. **58**, 415 (1936).
- (6) COHN, E. J., McMEEKIN, EDSALL, AND BLANCHARD: J. Am. Chem. Soc. **56**, 784 (1934).
- (7) COHN, E. J., McMEEKIN, EDSALL, AND WEARE: J. Am. Chem. Soc. **56**, 2270 (1934).
- (8) DALTON, J. B., AND SCHMIDT, C. L. A.: J. Biol. Chem. **103**, 549 (1933).
- (9) EDSALL: J. Am. Chem. Soc. **57**, 1506 (1935).
- (10) EDSALL: Private communication, January, 1938.
- (11) FALKENHAGEN: Electrolytes. The Clarendon Press, Oxford (1934).
- (12) FUOSS: J. Am. Chem. Soc. **58**, 982 (1936).
- (13) GIBSON: J. Am. Chem. Soc. **56**, 13 (1934).
- (14) GUCKER: Chem. Rev. **13**, 111 (1933).
- (15) GUCKER: J. Am. Chem. Soc. **56**, 1017 (1934).
- (16) GUCKER AND AYRES: J. Am. Chem. Soc. **59**, 447 (1937).
- (17) GUCKER AND AYRES: J. Am. Chem. Soc. **59**, 2152 (1937).
- (18) GUCKER, AYRES, AND RUBIN: J. Am. Chem. Soc. **58**, 2118 (1936).
- (19) GUCKER, GAGE, AND MOSER: J. Am. Chem. Soc. **60**, 2582 (1938).
- (20) HARNED AND EHLERS: J. Am. Chem. Soc. **55**, 2379 (1933).
- (21) International Critical Tables, 1st edition, Vol. III, p. 29. McGraw-Hill Book Co., Inc., New York (1926).
- (22) KIRKWOOD: J. Chem. Phys. **2**, 351 (1934).
- (23) LANGE: Fortschr. Chem. Physik physik. Chem. **19**, No. 6 (1928).
- (24) LANGE AND ROBINSON: Chem. Rev. **9**, 89 (1931).
- (25) LEIGHTON, P. A.: J. Am. Chem. Soc. **53**, 3017 (1931).
- (26) ORTEN, J. M., AND HILL, R. M.: J. Am. Chem. Soc. **53**, 2797 (1931).
- (27) PARKS, HUFFMAN, AND BARMORE: J. Am. Chem. Soc. **55**, 2733 (1933).
- (28) SCATCHARD AND KIRKWOOD: Physik. Z. **33**, 297 (1932).
- (29) SMITH, P. K., TAYLOR, A. C., AND SMITH, E. R. B.: J. Biol. Chem. **122**, 109 (1937).
- (30) WYMAN, J., JR.: J. Am. Chem. Soc. **56**, 536 (1934).
- (31) ZITTLE: Dissertation, University of California, 1934.
- (32) ZITTLE, C. A., AND SCHMIDT, C. L. A.: J. Biol. Chem. **108**, 161 (1935).

STUDIES IN THE PHYSICAL CHEMISTRY OF AMINO ACIDS, PEPTIDES, AND RELATED SUBSTANCES. XII

INTERACTIONS BETWEEN DIPOLAR IONS IN AQUEOUS SOLUTION¹

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I. INTRODUCTION

The class of molecules whose interactions we are considering here is characterized by having at least one positively charged and one negatively charged group in the neutral isoelectric state. Under these circumstances they do not move with the current and are therefore not ions in the sense of Faraday. They are, however, oriented by an electric field by virtue of their large dipole moments and may for convenience be called dipolar ions.

The simplest dipolar ion is glycine or aminoacetic acid. (Carbamic acid—aminoformic acid—does not exist in the free state in aqueous solution, although certain of its salts are stable.) It contains a positively charged NH_3^+ group and a negatively charged COO^- group, separated by a CH_2 group. The distance of separation is something over 3 Å. and the dipole moment therefore approximately 15 Debye units.

Other dipolar ions may differ from glycine by the number of NH_3^+ groups, of COO^- groups, or of CH_2 groups. The latter may increase the distance of separation between the positively and negatively charged groups, and therefore the dipole moment of the molecule, or this may remain the same, as in all α -amino acids which differ from each other in the length and configuration of their paraffin side chains. Dipolar ions may, however, contain still other groups. Thus amino acids bound to each other in peptide linkage contain one or more CONH groups, and the moments of di- and tri-peptides are greater than those of the simple amino acids. Peptides may also have paraffin side chains, sulfhydryl or hydroxyl groups, or other configurations possessed by the amino acids of which they are constituted.

Regardless of the complexity of their structure, the balance between two phenomena would appear to determine their behavior. Dipolar ions that

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are small in comparison with their moments have lower activity coefficients in more concentrated solutions. In this they resemble most ions. The resemblance goes further, for the effect upon the activity coefficient is smaller per mole the higher the concentration. Dipolar ions whose volumes are large in comparison with their moments generally have activity coefficients that are greater than unity. Moreover, the logarithm of the activity coefficient is essentially linear in the concentration. In this the behavior of such dipolar ions resembles that of many uncharged molecules.

The ratio of moment to volume thus renders the behavior of dipolar ions more comparable on the one hand to that of ions and, on the other, to that of uncharged molecules. This dichotomous behavior applies not only to the interactions of dipolar ions with each other but also to their interaction with ions. In early studies upon the solubility of amino acids in salt solutions (24, 23, 10) it was noted that neutral salts dissolved some amino acids and precipitated others. Among those dissolved was glycine; among those precipitated were leucine and tryptophane,—large amino acids which were “salted out.”

These solvent and precipitating actions of neutral salts had been noted with respect to the interaction of neutral salts and proteins long before they were noted for neutral salts and the amino acids of which proteins are constituted. In 1856 Denis noted that a fraction of the protein in blood was soluble in dilute salt solutions but not in water. In 1887 Hofmeister studied extensively the “salting-out” of proteins by electrolytes. These effects of salt are far greater in the case of proteins than of smaller dipolar ions and were therefore observed earlier. In order, however, to understand the nature of the molecular configurations which lead to changes in the activity coefficients of dipolar ions, we shall consider first smaller molecules of known structure.

II. SYSTEMS CONTAINING GLYCINE

Glycine

The influence of glycine in lowering the freezing point of aqueous solutions has been accurately investigated by Scatchard and Prentiss (28). Their results, calculated as activity coefficients at the freezing point, are given by the relation

$$-\log \gamma = 0.09910m - 0.01584m^2 \quad (1)$$

where m is concentration per 1000 grams of water. By means of the heat capacity and heats of dilution of Zittle and Schmidt (34) the above relation,² calculated by Scatchard for 25°C., yields

$$-\log \gamma = 0.08366m - 0.01507m^2 \quad (2)$$

² Gucker is investigating the heat capacities and the heats of dilution of glycine, alanine, and of certain related molecules, and his results when completed should lead to slight revision of these values.

The activity coefficients of glycine have also been determined by vapor pressure measurements by Smith and Smith (30) and by M. M. Richards (26), and their results are in good agreement as a first approximation³ with the freezing point determinations of Scatchard and Prentiss (28), with which they are compared in table 1.

TABLE 1
Activity coefficients of glycine in aqueous solution at 25°C.

GLYCINE CONCENTRATION		DIELECTRIC CONSTANT <i>D</i>	-LOG γ (SMITH AND SMITH (30), BY VAPOR PRESSURE)	-LOG γ (RICHARDS (26), BY VAPOR PRESSURE)	-LOG γ (SCATCHARD AND PRENTISS (28),* BY FREEZ- ING POINT)	-LOG γ (CALCU- LATED†)
<i>m</i>	<i>C</i>					
<i>moles per 1000 grams</i>	<i>moles per liter</i>					
0.1	0.099	80.8	0.0088		0.0082	0.0089
0.2	0.198	83.0	0.0168	0.0177	0.0161	0.0173
0.3	0.296	85.2	0.0241		0.0237	0.0252
0.4	0.393	87.4	0.0315	0.0330	0.0310	0.0326
0.5	0.489	89.6	0.0386		0.0381	0.0395
0.6	0.585	91.7		0.0463		0.0460
0.7	0.679	93.8	0.0516		0.0512	0.0521
0.8	0.773	96.0		0.0581		0.0578
1.0	0.958	100.1	0.0685	0.0686‡	0.0686	0.0684
1.2	1.140	104.2	0.0768	0.0780	0.0787	0.0780
1.4	1.318	108.3		0.0865		0.0863
1.5	1.406	110.3	0.0883		0.0916	0.0903
1.6	1.494	112.2		0.0941		0.0939
1.7	1.580	114.2	0.0964		0.0987	0.0976
1.8	1.666	116.1		0.1009		0.101
2.0	1.836	120.0	0.105	0.107	0.107	0.107
2.2	2.002	123.7		0.113		0.113
2.4	2.166	127.5		0.119		0.118
2.5	2.247	129.3	0.119			0.121
2.6	2.327	131.1		0.124		0.123
2.8	2.485	134.7		0.128		0.128
3.0	2.640	138.3	0.130	0.133		0.132
3.2	2.793	141.8		0.136		0.135
3.3	2.869	143.5	0.137			0.137

* Calculated for 25°C. by means of equation 2.

† Calculated by means of the equation: $-(\log \gamma)/C = K_R^* (D_0/D) - K_s^*$, where $K_R^* = 0.100$ and $K_s^* = 0.007$.

‡ This value is assumed equal to that of Scatchard and Prentiss at the same temperature and concentration (see reference 26, page 733).

There are several qualitative observations that may be made regarding these data: (a) as in the case of most electrolytes, the activity coefficients are less than unity; (b) unlike the case of electrolytes, $-\log \gamma$ varies in

³ See second footnote to table 1.

dilute solution with C and not with its square root; and (c) the ratio $-(\log \gamma)/C$ does not remain constant but diminishes with increasing concentration.

Glycine and asparagine

Glycine cannot be investigated in aqueous solutions by the solubility method. Most other α -amino acids are less soluble, but their paraffin side chains introduce strong repulsive forces to be considered subsequently. Asparagine is, however, an α -amino acid of low solubility and with no exposed CH_2 group. Moreover, the terminal group contains the CONH group, characteristic of the peptide linkage. Ammonia can be split from this group of asparagine and of the closely related glutamine in acid solution (1, 25), and the concentration of these amides in systems containing other amino acids can thus readily be investigated either by titration or by Nessler determination of the liberated ammonia.

The purification of asparagine offers some difficulty, as has been noted by several investigators (see, for instance, reference 29, page 489). Aspartic acid is usually present as an impurity and is best removed by carrying out the crystallizations at pH 6. Under these conditions salts of aspartic acid that are either present or formed during the processes of purification remain in the filtrate.

The asparagine used in these experiments was crystallized once from water and twice from 50 per cent ethanol. After drying in a desiccator to constant weight, it contained one molecule of water of crystallization. A saturated aqueous solution had a pH of 5.4, which is close to the isoelectric point as calculated from the dissociation constants, and the conductivity was 7×10^{-6} reciprocal ohms. Our preparations gave the theoretical value for amide nitrogen, namely, 9.33 per cent.

The solubility of asparagine was determined by the method of Pucher, Vickery, and Leavenworth (25). It was found necessary to increase the time of heating in acid to 20 hr. under the conditions of our experiments. Following our usual procedure (6), analyses were made after successive equilibrations of solvents with asparagine for approximately 24 hr. until the saturated solutions gave the same solubility for at least three successive days.

Most amino acids increase the solubility of asparagine, and the activity coefficients of the asparagine calculated from such measurements are given in table 2. The solubility increased from 0.184 mole per liter in water to only 0.192 in 1.5 molal alanine and decreased to 0.170 mole per liter in 1.5 molal α -aminobutyric acid. The greatest change in solutions of these two amino acids thus never exceeded 5 per cent, or approximately ten times the experimental error, whereas the same concentration of glycine increased solubility by more than 20 per cent. The results relating glycine

and asparagine have been plotted in figure 1 and compared with the various studies by freezing point and vapor pressure methods of the activity coefficient of glycine.

TABLE 2

Solubility of l-asparagine in aqueous amino acid solutions at 25°C.

AMINO ACID CONCENTRA- TION C_2	DENSITY OF SOLUTION ρ	DIELECTRIC CONSTANT OF SOLVENT D	SOLUBILITY OF <i>l</i> -ASPARAGINE		LOG N/N_0 (OBSERVED)	LOG N/N_0 (CALCULATED)
			C_1	N		
<i>l</i> -Asparagine in water						
moles per liter			moles per liter	mole fraction		
0.0	1.00714	78.5	0.184	0.00336		
<i>l</i> -Asparagine in glycine. $\delta = 22.6$; $K_R^* = 0.094$; $K_s^* = -0.006$						
0.25	1.01544	84.2	0.194	0.00357	0.026	0.023
0.50	1.02336	89.8	0.199	0.00370	0.042	0.044
1.00	1.03886	101.1	0.211	0.00397	0.073	0.079
1.50	1.05383	112.4	0.225	0.00430	0.107	0.108
2.00	1.06861	123.7	0.231	0.00449	0.126	0.132
2.80	1.09080	141.8	0.247	0.00494	0.167	0.163
<i>l</i> -Asparagine in diglycine. $\delta = 70.6$; $K_R^* = 0.136$; $K_s^* = -0.029$						
0.25	1.02164	96.2	0.196	0.00364	0.035	0.035
0.50	1.03508	113.8	0.201	0.00380	0.054	0.061
1.00	1.06120	149.1	0.218	0.00425	0.102	0.101
1.40	1.08170	177.4	0.224	0.00449	0.126	0.125
<i>l</i> -Asparagine in lysylglutamic acid. $\delta = 345$; $K_R^* = 0.150$; $K_s^* = -0.075$						
0.098	1.01762	112.4	0.186	0.00346	0.018	0.018
0.192	1.02780	144.8	0.189	0.00356	0.030	0.030
<i>l</i> -Asparagine in alanine. $\delta = 22.6$; $K_R^* = 0.094$; $K_s^* = 0.033$						
0.25	1.01436	84.2	0.188	0.00347	0.014	0.014
0.50	1.02132	89.8	0.191	0.00357	0.026	0.025
1.00	1.03490	101.1	0.192	0.00368	0.040	0.040
1.50	1.04788	112.4	0.192	0.00375	0.048	0.049
<i>l</i> -Asparagine in α -aminobutyric acid. $\delta = 22.6$; $K_R^* = 0.026$; $K_s^* = 0.012$						
0.25	1.01382	84.2	0.182	0.00338	0.003	0.003
0.50	1.02025	89.8	0.180	0.00339	0.004	0.005
1.00	1.03347	111.1	0.178	0.00346	0.013	0.008
1.50	1.04591	112.4	0.170	0.00342	0.008	0.009

At low concentrations the interaction of glycine with glycine and of glycine with asparagine would appear to yield almost identical activity

coefficients.⁴ The large size of the asparagine molecule does not appreciably diminish this effect, which might thus be thought to depend largely on the moments of these two dipolar ions. Both are α -amino acids, and the influence in increasing the dielectric constant of the solution due to glycine is reported to be somewhat larger than the comparable dielectric constant increment of asparagine, being 22.6 for glycine (33) and 20.4 for

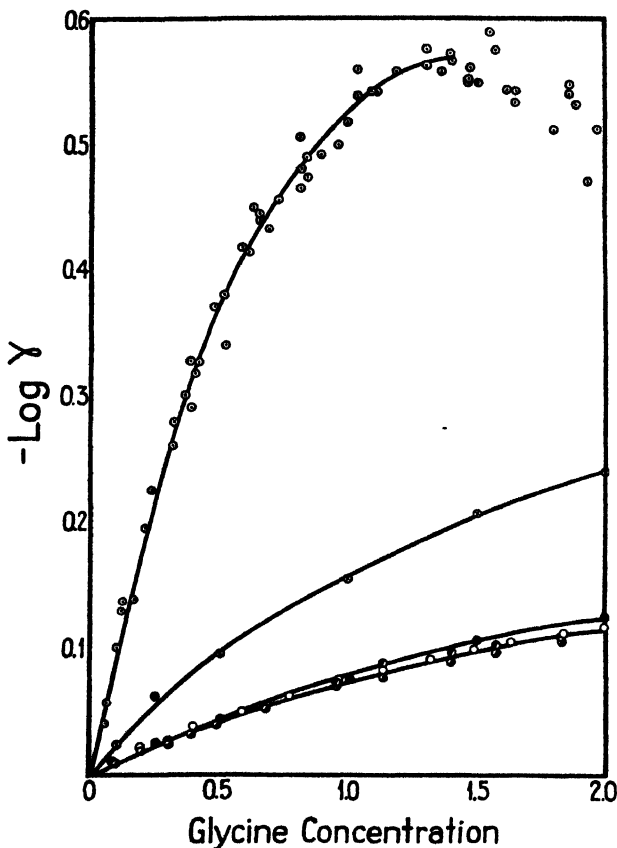


FIG. 1. Dipolar ions in glycine solutions. ○, glycine (Richards); ●, glycine (Scatchard and Prentiss); ⊙, glycine (Smith and Smith); ⊗, asparagine; ⊗, cystine; ○, hemoglobin (Richards).

asparagine (14), according to Wyman. This difference would appear to be greater than the experimental error and might be ascribable to the orienta-

⁴ In other respects also the physical chemical behavior of glycine and asparagine are superficially similar. Thus the change in free energy with change in solvent from water to ethanol at 25°C. of these two dipolar ions (6, 20) is almost identical; the values of $\log N_A/N_0$ for glycine and asparagine are, respectively, -3.391 and -3.402 .

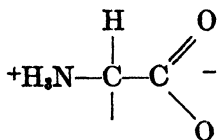
tion of the terminal amide group with respect to the dipolar ion moment, thus diminishing the total moment. The influence of glycine in diminishing the activity coefficient of asparagine is, however, not smaller but somewhat greater than the comparable effect of glycine upon glycine (figure 1). No correction has been made for the interaction of asparagine upon asparagine or for the influence of asparagine on the dielectric constant of the solution, though the solubility of asparagine is not completely negligible.

At higher glycine concentrations especially, the decrease in the activity coefficients of asparagine is greater than for glycine, suggesting the importance and desirability of further and more detailed comparative studies of dipolar ions which have nearly the same moments but the difference in whose volumes is not dependent on paraffin side chains.

Glycine and cystine

The interaction of glycine and the tetrapole cystine has been studied both in the presence and in the absence of electrolytes (4). The influence of one dipolar ion in decreasing the interaction between ions and the other dipolar ion has been stressed previously. In the present communication we are concerned rather with interaction between dipolar ions, and the logarithm of the activity coefficient of the cystine in the presence of varying concentrations of glycine is graphically represented in figure 1. Comparison of the curve for cystine with that for asparagine or glycine in glycine solutions indicates that *the largest factor in determining interaction between dipolar ions, as between ions and dipolar ions, is the magnitude of their electric moments.*

Cystine contains two positively charged ammonium groups, each in the α -position to a negatively charged dissociated carboxyl group. Differently stated, each molecule contains two configurations, each identical with that of glycine, asparagine, and other α -amino acids, the two



groups being connected by sulfur-sulfur linkage. Assuming free rotation between the



atoms which separate the two dipoles, the moment of each of which may be considered as approximately 15 Debye units, the moment of the cystine would be double this, or 30 Debye units, were the dipoles parallel, or zero

were they anti-parallel. From the interaction of cystine and neutral salts (21) it was concluded that the moment was somewhat smaller than if the dipoles were parallel but somewhat greater than could be expected on the basis of free rotation, and was tentatively placed between 23 and 28.5 Debye units. From the interaction of cystine and glycine another estimate of this moment could be deduced were the theory for the interaction of dipolar ions completely satisfactory.

Glycine and hemoglobin

A beautiful study of the influence of glycine on the solubility of hemoglobin has been reported within the year by M. M. Richards (26). The logarithms of the solubility ratios of hemoglobin reported by this investigator are plotted in figure 1 against the glycine concentrations as abscissa, without correcting for the influence of the hemoglobin upon the dielectric constant of the solution. The solubility of hemoglobin in the absence of glycine in these experiments varied from 13.9 to 17.8 g. per 1000 grams of water to over 60 g. per 1000 grams of water in 1.5 molal glycine. Since the dielectric increment per gram of hemoglobin may be taken as 0.33 (22), the dielectric constants of the saturated solutions were appreciably influenced by the protein as well as by the glycine. This effect had previously been considered with respect to the studies of Green (13) on the interaction of hemoglobin with sodium chloride in aqueous solution (3). Correcting for it would yield still greater estimates of activity coefficients due to Coulomb forces.

The curves relating $-\log \gamma$ and glycine concentration are very similar for the dipolar ions glycine and asparagine, for the tetrapolar ion cystine, and for the multipolar protein hemoglobin. In these studies the greater the interaction the greater the moments of the molecules. Thus the dipole moment of glycine and asparagine may be taken as 15, that of cystine as 27, and that of hemoglobin as 500 Debye units. These interactions are, as a first approximation, proportional to the first power of the moment, whereas theoretical considerations have suggested (12, 17) that they should be proportional to a higher power and diminish with increase in volume of the molecule on the basis of models which, it is true, cannot be expected satisfactorily to reproduce all the characteristics of dipolar ions.

In solutions of high dielectric constant the "salting-out" effect must also be considered in dipole-dipole interactions. This should be greater the greater the volume of the solute molecules, and lead to a larger correction for hemoglobin than for cystine, for cystine than for asparagine, and for asparagine than for glycine. This correction cannot, however, be made merely on the basis of the volume of the dipolar ion, but must take into account whether the side chains of the molecules are polar groups, as in the case of asparagine, or non-polar paraffin side chains, as in the case of

alanine, many other α -amino acids, and therefore many of the side chains of proteins.

III. SYSTEMS CONTAINING ALANINE

The electric moments of glycine and alanine are presumably identical, since alanine differs from glycine only by substitution of a hydrogen for a methyl group. The volume of the molecule is thus larger by one CH_2 group or by 16.3 cc. per mole (5) and the center of the dipole is presumably

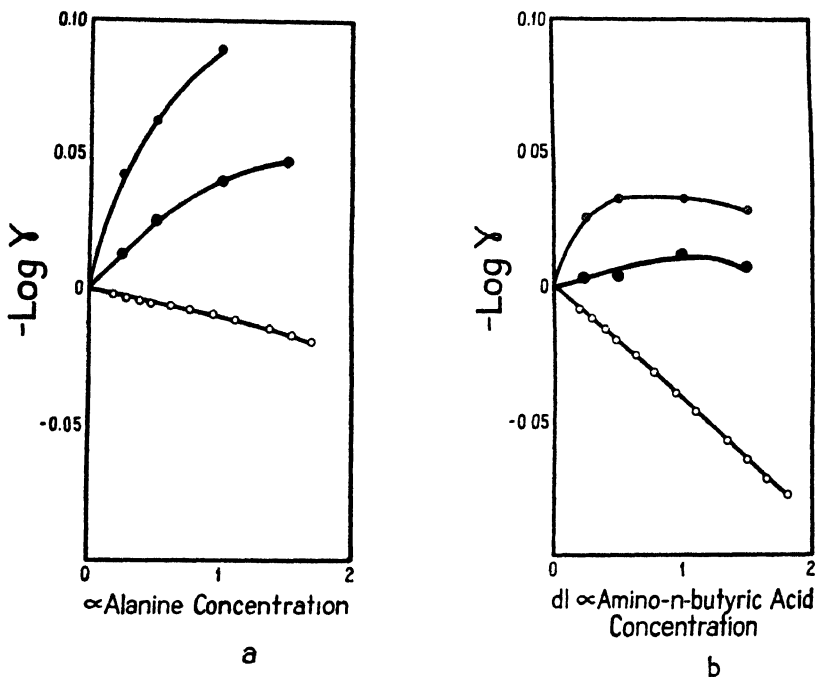


FIG. 2a. Dipolar ions in alanine solutions. \otimes , cystine; \bullet , asparagine; \circ , alanine
 FIG. 2b. Dipolar ions in α -aminobutyric acid solutions. \otimes , cystine; \bullet , asparagine;
 \circ , α -aminobutyric acid

farther from the center of the molecule than in the case of glycine (3, 18, 2). Interaction between alanine molecules has now been studied by measurements both of vapor pressure (31) and of freezing point (18). The vapor pressure measurements of Smith and Smith (31) are plotted in figure 2.

Whereas the activity coefficients of glycine, like those of electrolytes, are smaller than unity in dilute solution, those of alanine are greater. Moreover, $-(\log \gamma)/C$ is independent of alanine concentration,⁵ having a

⁵ Smith and Smith (30, 31) report concentration as grams per 1000 grams of water, m , and the ratio $-(\log \gamma)/m$, calculated from their results, diminishes with increase

value of -0.011 , as compared with a value for glycine (figure 1) which (a) is opposite in sign, (b) is nearly ten times as great as for alanine, and (c) diminishes with increase in concentration. If the effect for glycine is ascribed to the dipole moment of its molecules, then that for alanine must be ascribed to large repulsive forces due to its non-polar groups in aqueous solution. This effect is far greater if the side chain of an α -amino acid is an ethyl group, as in α -aminobutyric acid (figure 2b), and still greater if the paraffin chain is still longer, the slopes $-(\log \gamma)/C$ being -0.011 for *dl*-alanine (figure 2a), -0.043 for *dl*- α -aminobutyric acid (figure 2b), and -0.047 for *dl*- α -aminovaleric acid. Clearly the effect does not continue to increase at the same rate with further increase in the length of the paraffin side chain. It would appear to be somewhat greater for branched than for straight paraffin chains,⁶ according to the measurements of Smith and Smith (31), since the limiting slope is -0.054 for α -aminoisobutyric acid and -0.064 for *dl*-valine.

The salting-out effect due to interaction between amino acid molecules with paraffin side chains is far greater than can be accounted for in terms of the volume of the molecules. The apparent molal volume of α -aminoisobutyric acid is 78.1 cc., or almost identical with that of asparagine, 78.0 cc., and that of valine is still greater, 91.3 cc. (5).⁷ Regardless of size, all the molecules with methyl groups have activity coefficients greater than unity in their aqueous solutions—and presumably also in the presence of each other—whereas the activity coefficients of asparagine are less than unity in alanine solutions. Solubility studies on the basis of which these activity coefficients are calculated are reported in table 2 and graphically

in concentration. The concentration as moles per liter, C , has been estimated from the relation

$$m = 1000C/(1000 - \Phi C)997.08$$

where Φ , the apparent molal volume is $43.25 + 0.83C$ for glycine, $60.6 + 0.60C$ for alanine, and 76.5 for α -aminobutyric acid (7). The ratio $-(\log \gamma)/C$ yields salting-out constants independent of concentration for these amino acids.

* The change in free energy in the transfer from water to ethanol is also greater for branched-chain than for straight-chain amino acids. This is most readily demonstrated by adding the same increment 0.49 (K_1 in equation 3) for each CH_2 group.

	$\log N/N_0$	$\log N/N_0 + 0.49\mu_{\text{CH}_2}$
Glycine.....	-3.391	-3.391
Alanine.....	-2.856	-3.346
α -Aminobutyric acid.....	-2.375	-3.355
α -Aminocaproic acid.....	-1.414	-3.374
Valine.....	-2.158	-3.628
Leucine.....	-1.622	-3.582

the average of $(\log N/N_0 + 0.49\mu_{\text{CH}_2})$ being -3.37 for the straight-chain and -3.61 for the branched-chain α -amino acids.

represented in figure 2a. The limiting solvent slope of alanine upon asparagine may be taken as approximately 0.06 or far less than that for glycine.

IV. SYSTEMS CONTAINING α -AMINOBUTYRIC ACID

Comparison of figures 1, 2a, and 2b reveals the influence of each additional CH_2 group upon the interactions of α -amino acids and other dipolar ions. Whereas the activity coefficients of glycine and of asparagine in glycine are closely similar (figure 1), the small solvent actions of alanine upon cystine and asparagine may be contrasted with the salting-out effect of alanine on alanine. For α -aminobutyric acid these effects are still greater. All activity coefficients tend to become less negative or more positive, and cystine in α -aminobutyric acid shows the type of curve it exhibits in solutions of sulfates (21, 3) and that is characteristic of many proteins where decrease in activity coefficient in dilute solution is followed by directly observable salting-out effects in more concentrated solution.⁷

V. SYSTEMS CONTAINING ASPARAGINE

Terminal non-polar groups on interacting molecules have the opposite effect to that due to their electric moments. Thus alanine, α -aminobutyric acid, and valine have activity coefficients greater than unity in aqueous solution. On the other hand, alanine (figure 2a) and α -aminobutyric acid (figure 2b) diminish but do not reverse the effect due to their dipole moments in their interactions with asparagine. As a first approximation the CH_2 group possessed by alanine but not by glycine diminishes (table 2) $-(\log \gamma)/C$ by approximately 0.04 and the additional CH_2 group of α -aminobutyric acid by something over 0.04 with respect to alanine (figure 2b) or a total of nearly 0.09 with respect to glycine.

VI. SYSTEMS CONTAINING CYSTINE

The interactions not only of glycine and alanine but of α -aminobutyric acid and valine with cystine have also been studied by the solubility method (table 3). Here also the effect of increasing the length of the paraffin side chain is to diminish the solvent action of the α -amino acid. Taking the limiting slope of cystine and glycine (figure 1) as 0.23, of alanine (figure 2) as 0.16, of α -aminobutyric acid as 0.10, and of *dl*-valine as 0.06, *there would appear to be a nearly constant effect of each CH_2 group in diminishing the solvent action of dipolar ions of slightly less than 0.07 in $-(\log \gamma)/C$. It is thus possible that in the interactions of large molecules of high moment a decrease in $-(\log \gamma)/C$ of approximately 0.07 may be expected for each non-polar CH_2 group in paraffin side chains.*

Opposite in direction to the effect of paraffin side chains, in diminishing

⁷ Hemoglobin exhibits this effect in the most concentrated glycine solutions (26).

TABLE 3

Solubility of cystine in aqueous amino acid solutions at 25°C.

AMINO ACID CONCENTRA- TION C_2	DENSITY OF SOLUTION ρ	DIELECTRIC CONSTANT OF SOLVENT D	SOLUBILITY OF CYSTINE		LOG N/N_0 (OBSERVED)	LOG N/N_0 (CALCULATED)
			C_1	N		
Cystine in water						
moles per liter			moles per liter	mole fraction		
0.0	0.9972	78.5	0.000454	0.00000820		
Cystine in glycine. $\delta = 22.6$; $K_R = 0.293$; $K_s = 0.007$						
0.1	1.0020	80.8	0.000478	0.00000865	0.023	0.022
0.25	1.00512	84.2	0.000518	0.00000942	0.060	0.052
0.5	1.01279	89.8	0.000558	0.0000102	0.095	0.095
1.0	1.02801	101.1	0.000632	0.0000117	0.154	0.161
1.5	1.0422	112.4	0.000701	0.0000132	0.207	0.207
2.0	1.05755	123.7	0.000743	0.0000142	0.238	0.238
2.8	1.08033	141.8	0.000779	0.0000152	0.268	0.267
Cystine in diglycine. $\delta = 70.6$; $K_R = 0.380$; $K_s = 0.0$						
0.25	1.01097	96.2	0.000532	0.00000976	0.075	0.078
0.5	1.02446	113.8	0.000597	0.0000111	0.131	0.131
1.4	1.07164	197.4	0.000711	0.0000140	0.232	0.235
Cystine in urea.* $K_R = 0.085$; $K_s = 0.0$						
1.0	1.0133	81.3	0.000536	0.00000994	0.083	0.082
2.0	1.02852	84.0	0.000622	0.0000119	0.162	0.156
Cystine in <i>dl</i> -alanine. $\delta = 22.6$; $K_R = 0.293$; $K_s = 0.136$						
0.25	1.00431	84.2	0.000495	0.00000904	0.042	0.033
0.5	1.01139	89.8	0.000513	0.00000947	0.062	0.060
1.0	1.02529	101.1	0.000532	0.00001004	0.088	0.092
Cystine in α -aminobutyric acid. $\delta = 22.6$; $K_R = 0.293$; $K_s = 0.191$						
0.25	1.00408	84.2	0.000474	0.00000869	0.025	0.021
0.5	1.01082	89.8	0.000475	0.00000884	0.032	0.033
1.0	1.02435	101.1	0.000461	0.00000884	0.032	0.037
1.5	1.03764	112.4	0.000442	0.00000875	0.028	0.021
Cystine in <i>dl</i> -valine. $\delta = 22.6$; $K_R = 0.293$; $K_s = 0.234$						
0.25	1.00382	84.2	0.000454	0.00000835	0.008	0.010
0.5	1.01046	89.8	0.000453	0.00000849	0.015	0.011

* Values for D are taken from Wyman (32).

the interactions between dipolar ions in aqueous solution, is the influence of their electric moments. For cystine, as for asparagine, the solvent action is greater for diglycine than for glycine. For urea, with a moment of

approximately 5.1 Debye units (9), the very definite solvent action is less than for glycine. Moreover, as a *first approximation the change in free energy of interacting dipolar ions without paraffin side chains would appear to be proportional to the first power of their moments.*

VII. DISCUSSION

In considering the influence of various solvents upon the change in free energy of dipolar ions we have previously employed (6) the extensions of Debye's treatment for ions to the case of dipolar ions of Scatchard and Kirkwood (27) and of Kirkwood (16). Whether the shape of the dipolar ion be considered to be that of a dumb-bell, of a sphere, or of an ellipsoid, it appears that an additional term is required to account for the influence of the various groups of the dipolar ions. The change in free energy due to electrostatic forces ($\bar{F}_e - \bar{F}_e^0$) can be estimated from the observed activity coefficients, even as a first approximation, only after correction for the effects of these groups. An equation was therefore tentatively adopted with the form (6)

$$\bar{F}_e - \bar{F}_e^0 = -2.303kT (\log N/N_0 - K_1) = K_2 (1/D - 1/D_0) \quad (3)$$

in which K_1 is a constant related to non-electrostatic forces. K_1 has been shown to increase in series both of α -amino acids and of hydantoic acids for each additional CH_2 group in paraffin side chains ending in methyl groups by 0.23 for the transfer from water to formamide, by 0.44 to methanol, by 0.49 to ethanol and acetone, and by 0.53 to butanol and heptanol (3, page 245). If the values for K_1 be divided by the numbers of moles per liter in the pure non-aqueous solvents, these increments for each additional CH_2 group become 0.0092 for the transfer to formamide, 0.0179 to methanol, 0.0287 to ethanol, 0.0362 to acetone, 0.0487 to butanol, and 0.0751 to heptanol.

If we multiply $(1/D - 1/D_0)$ by $-D_0^2/\delta$, we have

$$-(D_0^2/\delta)(1/D - 1/D_0) = (D_0/D)(D - D_0)/\delta \quad (4)$$

The quantity δ in the above expression is the dielectric constant increment, defined by the relation $\delta = (D - D_0)/C$, which has been proven to hold for most dipolar ions by Hedestrand (15), Devoto (8), Wyman and McMee-kin (33), and others. For the interaction between dipolar ions it will be more convenient to substitute for $(D - D_0)/\delta$ in the last equation the concentration, C , in moles per liter of the dipolar ion. The change in free energy due to electrostatic forces can therefore conveniently be written for interactions involving dipolar ions in the form

$$-(\bar{F}_e - \bar{F}_e^0)/2.303kT = \log N/N_0 + K_e^*C = K_R^*(D_0/D)C \quad (5)$$

in which the salting-out constant K_R^* is equal to $-K_1/C$ and

$$K_R^* = K_2\delta/2.303D_0^2kT$$

On the basis of the above equation the logarithm of activity coefficients between dipolar ions should be linear in $(D_0/D)C$ in cases where the salting-

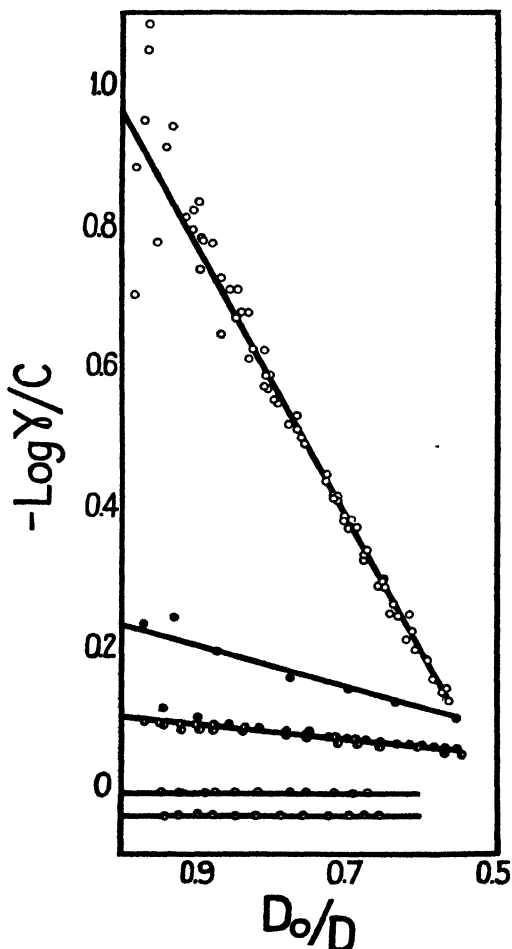


FIG. 3. Plot of $-(\log \gamma)/C$ against D_0/D . \circ , hemoglobin (Richards); \bullet , cystine; \otimes , glycine (Richards); \ominus , glycine (Scatchard and Prentiss); \bullet , glycine (Smith and Smith); \ominus , alanine (Smith and Smith); \ominus , α -aminobutyric acid (Smith and Smith).

out term is small. This is closely true for the interaction between asparagine and glycine (table 2) and between cystine and diglycine (table 3). In other cases, if this equation be valid and $(\log N/N_0)/C$ be plotted as ordinate against D_0/D as abscissa (figure 3), extrapolation to the point where D_0/D equals unity should yield $(K_R^* - K_s^*)$. The difference

TABLE 4
Constants for the interaction of dipolar ions

(1)	(2)	(3)	(4)	(5)	(6)		(7)	(8)	(9)	(10)	(11)	(12)	(13)
DIPOLAR ION	MOLAR VOLUME OF DIPOLAR ION	RADIUS OF DIPOLAR ION	DIPOLE MOMENT OF DIPOLAR ION	DISTANCE OF CLOSEST APPROACH	CONSTANT CALCULATED FROM DEPENDENCE ON DIELECTRIC CONSTANT OF MEDIUM		Sphere model K_R	CONSTANT CALCULATED FROM DIPOLE-DIPOLE INTER-ACTION	K_s	$K_R - K_s$	$-(\log \gamma)/C$	K_R^2	ESTIMATED FROM $\frac{D_0 K_R^2}{D} - K_s^2$
					Dumb-bell model K_R								
Interactions with one solute													
Interactions with asparagine ($\mu = 15$; $b = 3.31 \text{ \AA}$.)													
Glycine.....	57.0	2.82	15	5.64	0.43	0.35	0.053	0.022	0.031	0.098	0.100	0.007	
α -Alanine.....	73.3	3.08	15	6.16	0.43	0.35	0.041	0.022	0.019	-0.011		0.011	
α -Aminobutyric acid.....	89.6	3.29	15	6.58	0.43	0.34	0.033	0.022	0.011	-0.043		0.043	
α -Aminovaleric acid.....	105.9	3.46	15	6.92	0.43	0.34	0.029	0.022	0.007	-0.047		0.047	
Interactions with cystine ($\mu = 27$; $b = 3.94 \text{ \AA}$.)													
Glycine.....	57.0	2.82	15	6.13	0.43	0.34	0.042	0.021	0.021	0.100	0.094	-0.006	
Diglycine.....	93.3	3.34	26	6.65	1.36	1.06	0.097	0.043	0.054	0.165	0.136	0.029	
Lysylglutamic acid.....	211.5	4.37	59	7.68	6.63	5.20	0.343	0.122	0.221	0.225	0.150	-0.075	
α -Alanine.....	73.3	3.08	15	6.39	0.43	0.34	0.037	0.022	0.015	0.061	0.094	0.033	
α -Aminobutyric acid.....	89.6	3.29	15	6.60	0.43	0.34	0.033	0.022	0.011	0.014	0.026	0.012	
Interactions with hemoglobin ($\mu = 500$; $b = 27 \text{ \AA}$.)													
Urea.....	44.0	2.59	5	6.54	0.07		0.012	0.019	-0.007	0.088			
Glycine.....	57.0	2.82	15	6.76	0.56		0.101	0.037	0.064	0.226	0.293	0.067	
Diglycine.....	93.3	3.34	26	7.28	1.75		0.246	0.068	0.178	0.380	0.380	0.000	
α -Alanine.....	73.3	3.08	15	7.02	0.56		0.090	0.039	0.051	0.157	0.293	0.136	
α -Aminobutyric acid.....	89.6	3.29	15	7.23	0.56		0.081	0.040	0.041	0.102	0.293	0.191	
Valine.....	105.9	3.46	15	7.40	0.56		0.076	0.041	0.035	0.059	0.293	0.234	
Interaction with hemoglobin ($\mu = 500$; $b = 27 \text{ \AA}$.)													
Glycine.....	57.0	2.82	15	30		2.67	0.39	0.14	0.25	0.95	1.90	0.95	

^a Calculated from the assumption of spherical shape. The shapes of these molecules will be considered elsewhere (Cohn: Chem. Reviews, 1939). See also reference 3, table 5.

between this value and that where D_0/D equals 0.5 should yield $K_R^*/2$. In this way estimates of K_R^* and K_i^* for each interaction can be obtained, provided the experimental points fall on a straight line when plotted in this manner. Certain of the measurements reported are analyzed in this way in the final two columns of table 4. The limiting value of the slope, $-(\log \gamma)/C$, at zero concentration is conveniently given by $K_R^* - K_i^*$.

Theoretical calculations

Scatchard and Kirkwood have extended the treatment for the change in free energy with change in dielectric constant of the solvent to the case of dipolar ions (27). Considering a dipolar ion as made up of two spheres of radius b separated by a distance R , with a charge ϵz in one sphere and $-\epsilon z$ in the other, they evaluate $(\bar{F}_e - \bar{F}_e^0)/(1/D - 1/D_0)$ as $N\epsilon^2 z^2 (1/b - 1/R)$.

If we assume the last expression gives K_2 in equation 3, or $2.303D_0^2 kTK_R'/\delta$, where K_R' is analogous to the experimental K_R^* in equation 5, then when the solubility of a given dipolar ion is influenced by different substances, K_R' should increase directly with the dielectric constant increment, δ .

In order to test this equation we have tentatively assumed that R for glycine and all α -amino acids is 3.17 Å. Considering glycine to be a sphere of radius 2.82 Å. and the center of the dipole to be at the center of the molecule, the charges would be 1.24 Å. from the edge of the molecule (3, page 264). Taking b as 1.24 Å. throughout, values of K_R' , estimated on this "dumb-bell model," are given in column 6 of table 4.

This model does not allow for the volume occupied by parts of the molecule not situated between the charged groups. Kirkwood has developed a spherical model (16) within which any number of charges is located. The general expression for the change in free energy with the dielectric constant of the medium is in the form of an infinite series. However, for the special case of two charges equidistant from the center, an explicit summation has been made (2, equation 21). Taking the values of the radius b , given in column 3 of table 4, and assuming the distance of the charges from the edge to be 1.24 Å., as before, values of K_R' have been calculated⁸ and listed in column 7. Here too K_R' should, according to the theory, be proportional to δ .

In both these theoretical treatments the dipole molecules whose activity coefficients are considered are supposed to be surrounded by a structureless dielectric continuum, in which the presence of other dipolar ions increases the dielectric constant, their molecular structure being ignored. This picture may be replaced by one somewhat more detailed, which considers

⁸ For hemoglobin the two charges were taken as $2e$ and $-2e$, respectively, consistent with the dipole moment of 500 (22) and $R = 51.6$ Å. (see Ferry, Cohn, and Newman: J. Am. Chem. Soc. 60, 1480 (1938)).

molecular interaction of pairs of dipolar ions immersed in a supposedly continuous medium with the dielectric constant of the pure solvent. Here the greater complexity of the treatment has led to a simpler model for the dipolar ion. In the development of Fuoss (11, 12) the molecule is represented by a sphere of radius b with a point dipole at the center.⁹ Following Fuoss, the interaction constant of a dipole species i in the presence of an excess of a species k in water at 25°C. is given by

$$K_R = -(\log \gamma_i)/C_k = 3.69 \times 10^{-4} \mu_i \mu_k \theta(x) \quad (6)$$

where μ_i and μ_k are the moments of the two dipoles in Debye units and $\theta(x)$ is a function given by Fuoss (12, table 2), where

$$x = 0.706 \mu_i \mu_k / (b_i + b_k)^3$$

and b_i and b_k are the radii of the two dipoles. Here both x and K_R , as given by Fuoss, have been multiplied by the factor 9/4, in accordance with the correction of Kirkwood (17, 18) for the case that the dielectric constant of the cavities represented by the molecules is small compared with that of the surrounding solvent.

Dipole interaction has been calculated by means of the above equation for the molecules that have been investigated, using the values of μ and b given in table 4. These values of K_R are listed in column 8.

In order to account for the salting-out effect in dipole-dipole interaction, Kirkwood (18) has suggested for the same spherical model an equation of the form

$$K_s = \frac{3\pi N}{2303 D k T} \frac{1}{2(b_i + b_k)^3} (\mu_i^2 b_k^3 + \mu_k^2 b_i^3) \quad (7)$$

which for water at 25°C. becomes

$$K_s = [3.82 \times 10^{-4} / (b_i + b_k)^3] [\mu_i^2 b_k^3 + \mu_k^2 b_i^3] \quad (8)$$

Values of K_s calculated on the basis of this equation are listed in column 9, and the differences $K_R - K_s$, representing theoretical limiting slopes, are in column 10 of table 4.¹⁰

Comparison of theory with experiment

These various calculations may now be compared with the experimental limiting slopes in column 11 of table 4. The only cases in which there is

⁹ This simple model may be also used in the calculation of the change of free energy with dielectric constant; it yields values of K_R' somewhat smaller than those in column 7, owing to suppression of terms in the multipole moments which are included in the two-charge model of Kirkwood.

¹⁰ An alternative molecular model suggested by Kirkwood (18) for calculations of interaction of elongated dipoles is that of a rod joining two charges. The interaction constant K_R for water at 25°C. is $0.167 R_2 (1 - R_2/3R_1)$, where R_1 and R_2 are the larger and smaller dipole distances, respectively, of the two species of dipolar ions. This yields for K_R a value of 0.35 for all α -amino acids,—a figure far higher than estimated for spherical dipoles, owing to neglect of molecular volume.

even approximate agreement with the Born-Fajans treatment are those of cystine in urea and hemoglobin in glycine. In each of these systems the molecule whose solubility is measured is large compared with the other dipolar ionic species, so that the merging of the latter in a continuous medium, assumed by the theory, is more closely approached. In all other systems investigated the calculated values are many times larger than those observed, the discrepancy being greater for the dumb-bell than for the spherical model.

Corrected or uncorrected for the salting-out effect, the model for interaction between spherical molecules with dipoles at their centers gives far smaller results, more nearly of the order of the experimentally observed limiting slopes (column 11). Two types of discrepancy are apparent. For the activity coefficients of glycine, asparagine, cystine, and hemoglobin in glycine, diglycine, and lysylglutamic acid, the calculated limiting slope is too small; presumably the dipoles are mutually accessible to a greater extent than represented by the model. On the other hand, for the activity coefficients of α -amino acids with paraffin side chains and for asparagine in α -aminobutyric acid, the calculated limiting slope is too large; presumably the repulsive effect of the side chains is greater than the model represents.

While the agreement of the different theoretical approaches with experiment is nowhere satisfactory, the nature of the discrepancies suggests that a much better representation of the facts may be obtained by extending the treatment of dipole-dipole interaction to molecular models of a more detailed and specific structure.

Conclusions from experiments

The experimental data give the opportunity of making certain further generalizations. Thus the observed activity coefficients are in some cases less, in others greater, than unity. Those calculated (columns 6 to 10) are, however, all less than unity regardless of which model is considered, except in the case of cystine in urea (column 10). Here, however, the observed limiting slope is positive and is given satisfactorily as a first approximation, as we have seen, by the Born-Fajans treatment.

Thus the activity coefficients of alanine, α -aminobutyric acid, and α -aminovaleric acid are most readily described in terms of the salting-out constant K_s^* , having the values listed in the last column of table 4. *Large values of K_s^* have been observed in all interactions in which one or both dipolar ions have paraffin side chains*, and the values of K_s^* are, moreover, of the same order of magnitude as for the transfer to non-aqueous solvents.

In contrast to the influence of the paraffin side chain upon K_s^* is that of an amide or peptide group. We have estimated that K_s^* was close to zero in the interaction between glycine and asparagine on the basis of

equation 5, and asparagine has an amide group. K_* has also been estimated to be zero for the interaction of diglycine and cystine, and diglycine contains the peptide linkage. In the interaction between asparagine and diglycine, or asparagine and lysylglutamic acid, *where amide and peptide groups are constituent parts of both interacting dipolar ions, K_* appears to have a sign opposite to that observed for the other dipolar ions investigated.* This is reminiscent of studies upon such molecules as succinic acid (19), for which a linear relationship between "salting-in" by certain electrolytes and the concentration has been observed.

The moments for glycine, diglycine, and lysylglutamic acid are 15, 26, and 59 Debye units, respectively. The observed limiting slopes for the interaction of asparagine with these three dipolar ions may be taken as 0.10, 0.17, and 0.23. Thus K_R^* increases by less than the first power of the moment. The interaction of cystine has been studied with urea, glycine, and diglycine, and their moments may be taken as 5.1, 15, and 26, or roughly as 1 is to 3 is to 5. The observed limiting slope for urea, 0.088, is less than a third smaller than that for glycine, and that for diglycine, 0.380, is less than five times that for urea. As in the case of interactions with asparagine, *interactions between the dipolar ions that have been investigated indicate that change in free energy with change in moment increases by slightly less than the first power of the products of the moments.*

VIII. SUMMARY

1. Interactions between dipolar ions in aqueous solution are considered.
2. The activity coefficients of glycine in aqueous solution are approximately given by the equation

$$-(\log \gamma)/C = K_R^*(D_0/D) - K_*$$

where $K_R^* = 0.10$ and $K_* = 0.007$ at 25°C.

3. The activity coefficients of α -amino acids with paraffin side chains are all greater than unity, and are given by the equation

$$(\log \gamma)/C = K_*$$

where K_* is equal to 0.011 for alanine, 0.043 for α -aminobutyric acid, and 0.047 for α -aminovaleric acid.

4. The activity coefficients of asparagine, an α -amino acid whose side chain terminates in an amide group, are less than unity in solutions of the other amino acids and peptides studied. In glycine K_R^* , in the above equation, is 0.094, and K_* is -0.006 ; in diglycine and peptides of larger moment, though K_R^* is greater, K_* also appears to be negative.

5. The double dipole, cystine, has both a larger moment and a larger volume than the other α -amino acids investigated, and its activity coefficients in glycine are given by putting K_R^* equal to 0.293 and K_* to 0.067.

In the presence of other dipolar ions K_R^* is greater if their dipole moment is greater, and K_s^* is greater if they contain paraffin side chains.

6. In the interactions of cystine and other dipolar ions, K_R^* appears to vary more nearly with the first than with the second power of the moment.

7. The observed limiting slopes are compared with calculations based on various models for dipolar ions.

REFERENCES

- (1) CHIBNALL, A. C., AND WESTALL, R. G.: *Biochem. J.* **26**, 122 (1932).
- (2) COHN, E. J.: *Ann. Rev. Biochem.* **4**, 93 (1935).
- (3) COHN, E. J.: *Chem. Rev.* **19**, 241 (1936).
- (4) COHN, E. J., McMEEKIN, T. L., AND BLANCHARD, M. H.: *Compt. rend. trav. lab. Carlsberg, Sørensen Jubilee Volume*, **22**, 142 (1938); *J. Gen. Physiol.* **21**, 651 (1938).
- (5) COHN, E. J., McMEEKIN, T. L., EDSALL, J. T., AND BLANCHARD, M. H.: *J. Am. Chem. Soc.* **56**, 784 (1934).
- (6) COHN, E. J., McMEEKIN, T. L., EDSALL, J. T., AND WEARE, J. H.: *J. Am. Chem. Soc.* **56**, 2270 (1934).
- (7) DANIEL, J., AND COHN, E. J.: *J. Am. Chem. Soc.* **58**, 415 (1936).
- (8) DEVOTO, G.: *Gazz. chim. ital.* **60**, 520 (1930); **61**, 897 (1931); *Z. Elektrochem.* **40**, 490 (1934).
- (9) DEVOTO, G.: *Gazz. chim. ital.* **63**, 491 (1933).
- (10) EULER, H. VON, AND RUDBERG, K.: *Z. physiol. Chem.* **140**, 113 (1924).
- (11) FUOSS, R. M.: *J. Am. Chem. Soc.* **56**, 1027 (1934).
- (12) FUOSS, R. M.: *J. Am. Chem. Soc.* **58**, 982 (1936).
- (13) GREEN, A. A.: *J. Biol. Chem.* **95**, 47 (1932).
- (14) GREENSTEIN, J. P., AND WYMAN, J., JR.: *J. Am. Chem. Soc.* **58**, 463 (1936).
- (15) HEDESTRAND, G.: *Z. physik. Chem.* **136**, 36 (1928).
- (16) KIRKWOOD, J. G.: *J. Chem. Phys.* **2**, 351 (1934).
- (17) KIRKWOOD, J. G.: *Chem. Rev.* **19**, 275 (1936).
- (18) KIRKWOOD, J. G.: Personal communication.
- (19) LINDERSTRØM-LANG, K.: *Compt. rend. trav. lab. Carlsberg* **15**, No. 4 (1924).
- (20) McMEEKIN, T. L., COHN, E. J., AND WEARE, J. H.: *J. Am. Chem. Soc.*, **57**, 626 (1935); **58**, 2173 (1936).
- (21) McMEEKIN, T. L., COHN, E. J., AND BLANCHARD, M. H.: *J. Am. Chem. Soc.* **59**, 2717 (1937).
- (22) ONCLEY, J. L.: *J. Am. Chem. Soc.* **60**, 1115 (1938).
- (23) PFEIFFER, P., AND ANGERN, O.: *Z. physiol. Chem.* **133**, 180 (1924).
- (24) PFEIFFER, P., AND WÜRGLE, J.: *Z. physiol. Chem.* **97**, 128 (1916).
- (25) PUCHER, G. W., VICKERY, H. B., AND LEAVENWORTH, C. S.: *Ind. Eng. Chem.* **7**, 152 (1935).
- (26) RICHARDS, M. M.: *J. Biol. Chem.* **122**, 727 (1938).
- (27) SCATCHARD, G., AND KIRKWOOD, J. G.: *Physik. Z.* **33**, 297 (1932).
- (28) SCATCHARD, G., AND PRENTISS, S. S.: *J. Am. Chem. Soc.* **56**, 2314 (1934).
- (29) SCHMIDT, C. L. A.: *The Chemistry of the Amino Acids and Proteins*. Charles C. Thomas, Springfield, Illinois (1938).
- (30) SMITH, E. R. B., AND SMITH, P. K.: *J. Biol. Chem.* **117**, 209 (1937).
- (31) SMITH, P. K., AND SMITH, E. R. B.: *J. Biol. Chem.* **121**, 607 (1937).
- (32) WYMAN, J., JR.: *J. Am. Chem. Soc.* **55**, 4116 (1933).
- (33) WYMAN, J., JR., AND McMEEKIN, T. L.: *J. Am. Chem. Soc.* **55**, 908 (1933).
- (34) ZITTLE, C. A., AND SCHMIDT, C. L. A.: *J. Biol. Chem.* **108**, 161 (1935).

ELECTROSTATIC INTERACTION OF MOLECULES¹

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In the electrostatic theory of crystals and liquids the existence of an additive lower bound for the electrostatic energy is generally taken for granted as a very trivial matter, and it does not appear that a rigorous proof, even for a simplified model, has ever been attempted. For an assembly of ions or even electric dipoles, a computation of the Coulomb energy by direct summation meets with considerable difficulty because the convergence is conditional at best, and the sequence of summation must be considered with some care even in the case of a perfect crystal lattice. However, it is easy to show that for no assembly of ions is there an *additive upper bound* for the energy: Consider the cations stacked in one pile, and the anions in another!

The idea of a lower bound for the electrostatic energy *per se* cannot be separated from the assumption of a closest distance of approach between the centers of charges. We shall therefore restrict our considerations to "hard billiard ball" models of molecules and ions, and attempt no more refined representation of the short-range repulsive forces. There need be no restriction as to the shape of the "billiard balls"; only the hardness is essential, and the particles may have a dielectric constant, or even more general assumptions about their polarizability are admissible.

To obtain a lower bound for the electric energy of an assembly of such particles, let us imagine that we have on hand a large quantity of a continuous conducting fluid. According to electrostatics, the energy released by the immersion of a charged body in such a fluid is finite; we shall call it the *proper energy* of the particle i (species). Without risk of confusion, this proper energy may be denoted simply by u_i , for we shall have no other occasion to assign energies to individual particles. The energy of interaction between any two particles we shall denote by u_{ik} .

Consider all the particles of our assembly immersed one at a time in our conducting fluid. When all the particles are immersed, the energy of the whole system equals

$$- \sum u_i$$

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regardless of the arrangement of the particles. Now the removal of the fluid cannot release any more energy; on the contrary, some energy must in general be expended to accomplish it. Thus, however the particles may be arranged, we know a lower bound for the energy:

$$U = \sum u_{ik} \geq - \sum u_i \quad (1)$$

For an ion of charge e and radius a , the proper energy is given by the familiar formula

$$u_i = e^2/2a$$

and equals the total Maxwell energy of the external field of the ion:

$$u_i = e^2/2a = \frac{1}{8\pi} \int_{r>a} \text{grad}^2 (e/r) 4\pi r^2 dr \quad (2)$$

For a permanent dipole of strength μ possessed by a particle of radius a and polarizability

$$\alpha = a^3(\epsilon - 1)/(\epsilon + 2) \quad (3)$$

we find

$$\begin{aligned} u_i &= \mu^2/2(a^3 - \alpha) = (\epsilon + 2) \mu^2/6a^3 \\ &= \frac{1}{8\pi} \int_{r>a} \text{grad}^2 (\mu \cos \theta/r^2) dV + \frac{\epsilon}{8\pi} \int_{r<a} \text{grad}^2 (\mu r \cos \theta) dV \end{aligned} \quad (4)$$

Here not only the external field energy

$$\mu^2/3a^3$$

of the electric dipole, but an additional amount

$$\epsilon\mu^2/6a^3 = (a^3 + 2\alpha)/6a^3(a^3 - \alpha)$$

of *internal energy* is released by the immersion of the particle in a conductor. Thereby the electric moment increases in the ratio

$$\mu_\infty/\mu_0 = (\epsilon + 2)/3 = a^3/(a^3 - \alpha) \quad (5)$$

In general, for a multipole described by a spherical harmonic of order n in a spherical particle of effective dielectric constant ϵ , the ratio of internal and external energies will be

$$u_{\text{int}}/u_{\text{ext}} = n\epsilon/(n + 1) \quad (6)$$

and the strength of the multipole increases by immersion, in the ratio

$$M_\infty^{(n)}/M_0^{(n)} = (n\epsilon + n + 1)/(2n + 1) \quad (7)$$

The lower bound given by equation 1 cannot, in general, be realized. It is of interest to see how closely it can be approached by arrangements consistent with the models.

For a given type of ionic lattice the electric energy depends on the minimum distance between anion and cation, but the proper energies of the ions involve the radius of each ion. To render the question definite, we shall compare the lattice energy with least proper energy which is consistent with a given mean diameter r_0 of the ions:

$$a_+ + a_- = r_0 \quad (8)$$

For a compound, $C_n^{(m+)} A_m^{(n-)}$, the self energy is

$$\sum u_i = e^2 \left(n \frac{m^2}{2a_+} + m \frac{n^2}{2a_-} \right) \quad (9)$$

The minimum of this quantity under the restriction 8 is obtained when

$$\frac{e_+}{a_+^2} + \frac{e_-}{a_-^2} = \frac{m}{a_+^2} - \frac{n}{a_-^2} = 0 \quad (10)$$

and equals

$$\text{Min}(\sum u_i) = mn(\sqrt{m} + \sqrt{n})^2/2r_0 \quad (11)$$

We obtain for ionic compounds CA , CA_2 , and C_2A_3 , respectively,

$$1.1(1 + 1)^2/2 = 2$$

$$1.2(1 + \sqrt{2})^2/2 = 3 + 2\sqrt{2} = 5.82843 \quad (12)$$

$$2.3(\sqrt{2} + \sqrt{3})^2/2 = 15 + 6\sqrt{6} = 29.6969$$

In table 1 the energies of some important lattices, taken partly from Born and Goeppert-Mayer (1) and partly from Sherman (4), are expressed in fractions of the least proper energies. Lattice types marked by an asterisk have adjustable parameters which have been chosen so as to give the lowest possible electrostatic energy.

Lattices made up of identical dipole molecules involve the complications of polarizability and of possible resultant electric moments.

On account of the polarizability, the moment of a molecule in the lattice will be

$$\mu = \mu_0 + \alpha E \quad (13)$$

where E is the electric field due to the other molecules. (In the lattices which we shall consider here, the directions of μ and E are parallel.) The field E is, of course, proportional to the actual moments μ , but the energy will be

$$\sum u_{ik} = -\frac{1}{2}NE\mu_0 \quad (14)$$

The ratio E/μ is given by the geometry of the lattice. We shall assume spherical molecules of radius a , and characterize the type of lattice by the dimensionless ratio γ , defined by the equation

$$E = \gamma\mu/a^3 \quad (15)$$

Then the lattice energy will be

$$\begin{aligned} U = \sum u_{ik} &= -\frac{1}{2}N\mu_0^2\gamma/(a^3 - \gamma\alpha) \\ &= -\sum u_i \times \gamma(a^3 - \alpha)/(a^3 - \gamma\alpha) \end{aligned} \quad (16)$$

Here equation 1 implies $\gamma \leq 1$. For "electret" arrangements in which the crystal has a net electric moment per unit volume, the electric field *outside the crystal* due to this moment will in general contain an energy comparable to the total proper energy of the molecules, but dependent on the shape of

TABLE 1

Energies of some important lattices expressed in fractions of the least proper energies

LATTICE	SYSTEM	COORDINATION NUMBER	$-\sum u_{ik}/\sum u_i$
Cesium chloride, CsCl.....	Cubic	8	0.8813
Sodium chloride, NaCl.....	Cubic	6	0.8738
Zinc blende, ZnS.....	Cubic	4	0.8190
Wurtzite, ZnS.....	Hexagonal	4	0.8197
Calcium fluoride, CaF ₂	Cubic	4-8	0.8645
Rutile, TiO ₂	Tetragonal*	3-6	0.8263
Anatase, TiO ₂	Tetragonal*	3-6	0.8236
Cuprite, Cu ₂ O.....	Cubic	2-4	0.7061
Corundum, Al ₂ O ₃	Hexagonal*	4-6	0.8429

* Parameters adjusted to optimum values.

the crystal and negligible for a very long needle polarized lengthwise (5). Other ways to eliminate the external field are twinning—a common habit of ferromagnetic crystals—or the immersion in a conductor. Any such device which reduces the boundary effectively to an equipotential will lead to a periodic potential (not merely a periodic field) in the interior of the crystal, and to a minimum energy which will be referred to as the energy of the electret.

For certain particularly simple cubic lattices, known as *diagonal lattices* (1), the energy can be computed very simply from a classical consideration of symmetry. In such cases the energy equals

$$U = -\frac{4\pi}{3} N\mu^2/2 \quad (17)$$

where N is the number of dipoles per unit volume. The important characteristic of a diagonal lattice is that four trigonal axes of symmetry pass

through every occupied point. In table 2 the constant γ defined by equation 15 has been computed for some important electret lattices and for simple linear, quadratic, and cubic lattices of dipoles arranged so that the orientations of nearest neighbors are reflected in the line connecting them. The energies of the "reflected" lattices and the energy differences between hexagonal and cubic electrets have been computed by an adaptation of Madelung's method (2). Some other lattices of alternating orientations have been discussed by Van Vleck (5). Arrangements of alternating orientations have not been listed for coordination numbers greater than 6, because none has been found of energies lower than those of the corresponding electrets. It seems a safe conjecture that the hexagonal close-packed lattice, completely polarized in the direction of the major axis, has a lower energy than any other arrangement of spheres carrying electric

TABLE 2
Values of γ computed for some lattices

LATTICE	COORDINATION NUMBER	γ^*	γ^\dagger
A. Electrets:			
Close-packed cubic	12	$\pi\sqrt{2}/6 =$	0.7405
Close-packed hexagonal	12	0.7413	0.7400
Simple cubic	6	$\pi/6 =$	0.5236
Cube-centered	8	$\pi\sqrt{3}/8 =$	0.6802
Diamond	4	$\pi\sqrt{3}/16 =$	0.3401
Ice	4	0.3485	0.3359
B. Reflected orientations:			
Simple cubic	6	0.6692	
Simple quadratic	4	0.6374	0.3307
Linear	2	0.601	0.225

* Dipoles oriented parallel to major axis or plane.

† Dipoles oriented perpendicular to major axis or plane.

dipoles. However, if for some reason the dipoles are arranged in the 6-coordinated simple cubic lattice, or in one of the 4-coordinated lattices, then lower energies can be attained by "reflected" orientations. For the simple cubic lattice one can easily show that arrangements of reflected orientation have the lowest possible energy. The proof depends on the observation that the entire space of the crystal can be divided by plane equipotential surfaces into cubes, each containing one dipole at the center, so that the energy of the lattice will be the same as if the dipoles, however oriented, were enclosed in individual Faraday cages. For the 4-coordinated diamond and ice lattices, it is also possible to find arrangements of lower energies than the electrets. The value of γ for a zigzag string with tetrahedral angles is 0.43 when the dipoles are oriented lengthwise, and the *average* value of γ for all arrangements of such strings in a given lattice is

necessarily the same; the maximum of γ for these lattices is probably not far from 0.53.

The comparison between electrets and other arrangements is of interest to the theory of dielectrics, because the temperature coefficient of the dielectric constant and the possibility of a Curie point depend on the relative energies of polarized and unpolarized states. The contrast between dense and loose packings may be general.

Tables 1 and 2 show that, in favorable cases, the lower bound given by equation 1 is a remarkably close one. It is easy to understand that the proper energies of ions can be released more completely than those of dipoles. The electrostatic energy of ions is all contained in their external fields, but in the case of dipoles at least one-third of the energy is internal, and even their external energy is more closely confined.

It has been shown that the fraction of the proper energy released by the formation of an ionic lattice depends on the ratio of the diameters of the ions. For the optimum, equation 10 requires equality of the *surface field intensities* of the ions. This condition is rather imperfectly realized in nature, for cations tend to be small while anions tend to be large, and more so the greater the valence of either. That highly charged ions get along better than they should on the basis of our considerations depends on the shortcomings of the ionic model when applied to cases which really represent a transition between ionic and homopolar interaction.

Chemical evidence indicates that in spite of the oversimplification of the model, the condition expressed by equation 10 has something to do with the relative stability and solubilities of ionic compounds, although in typical stable insoluble salts the cations have generally stronger fields than the anions. This may be just a matter of competition in a world of small cations and large anions, or else indicate a measure of homopolar character inherent in all ionic interaction.

The "matching condition" for the surface fields is at least capable of characterizing those liquids which are good solvents for electrolytes, namely, those polar liquids whose molecular surface fields are as intense as the fields of the ions. For a spherical dipole the maximum intensity of the surface field equals

$$E = 2\mu/a^3$$

If this is the decisive characteristic, then the solvent power for electrolytes is by no means a function of the dipole moment μ alone, nor of the proper energy

$$u_i \sim \mu^2/a^3$$

nor of the dielectric constant,

$$D \sim u_i/kT$$

Instead, among two liquids of the same dielectric constant, the one of lower molecular volume will generally have the greater ability to dissolve electrolytes. However, it will be obvious that localization of the surface field will have the same effect as a small molecular volume. A comparison of these conclusions with experience would amount to a reiteration of the outstanding empirical rules.

Since the surface field of a molecule depends on induction from the environment, it seems worth while to indicate a scheme of description which eliminates some of the resultant complications. There are many possible arrangements of charges in the interior of a particle which will give rise to the same external field, but there is exactly one distribution of charges over the surface which will produce a given field. For an ion of spherical symmetry, charge e and radius a , the required charge density is obviously

$$\sigma = e/4\pi a^2 \quad (18)$$

A spherical dipole molecule carries the fixed charge distribution

$$\sigma = 3\mu_\infty \cos \theta / 4\pi a^3 = 3\mu_0 \cos \theta / 4\pi (a^3 - \alpha) \quad (19)$$

in the notation of equation 5. In addition to these fixed charges, *there are induced charges whenever the surface is not an equipotential*. For an isolated dipole molecule, the induced surface charge equals

$$\sigma_{\text{ind}} = -3\alpha\mu_\infty \cos \theta / 4\pi a^6$$

so that the total electric moment is μ_0 instead of μ_∞ . The generalization to higher multipoles is obvious.

In this scheme of description the condition for minimum energy is the best possible compensation of neighboring surface charges.

As an illustration we may construct an electrostatic model of the water molecule which will account for the known structure of the ice lattice, including the type of randomness assumed by Pauling (3). The shape of the molecule may be spherical, and the charge distribution may consist of fairly concentrated positive charges near two corners of an inscribed tetrahedron and similar negative charges near the other two corners. If such molecules are arranged in a lattice of tetrahedral coordination and oriented so that positive and negative charges compensate each other at all points of contact, practically the whole proper energy of the molecules will be released. According to Pauling's estimate, there are $(3/2)^N$ ways of orienting N molecules with matching of the charges, and from the agreement with the observed residual entropy of ice, he infers that those $(3/2)^N$ configurations have all about the same energy. This hypothesis would indeed be true on the basis of our model, for when the compensation of adjacent charges is perfect, there are no stray fields left.

Incidentally, it is possible to show that the number of Pauling's "configurations" is larger than $(3/2)^N$, but a tentative estimate of the correction indicates that it is well within the experimental error of the residual entropy.

While our purely electrostatic model of a "proton bond" may need refinements, the general scheme would seem to accomodate them readily.

REFERENCES

- (1) BORN, M., AND GOEPPERT-MAYER, M.: *Handbuch der Physik*, 2nd edition, XXIV/2. Julius Springer, Berlin (1933).
- (2) MADELUNG: *Physik. Z.* **19**, 524 (1918).
- (3) PAULING, L.: *J. Am. Chem. Soc.* **57**, 2680 (1935).
- (4) SHERMAN, J.: *Chem. Rev.* **11**, 93 (1932).
- (5) VAN VLECK: *J. Chem. Phys.* **5**, 556 (1937).

ENERGY AND VOLUME RELATIONS IN THE SOLUBILITIES OF SOME KETONES IN WATER^{1,2}

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A study has been made in this laboratory of the solubility in water of several series of slightly soluble organic compounds. Such systems are sufficiently dilute so that but little interaction is to be anticipated between the solute molecules themselves. They thus afford an opportunity to study the interactions between the solvent water molecules and the organic molecules as reflected in the solubility values and their change with temperature, and in the energy values associated with the solution process.

The solubilities of several simple series of compounds, including aromatic hydrocarbons and halogenated aliphatic and aromatic hydrocarbons, have been measured, as well as of the series of aliphatic ketones for which data are given here. The ketones, while showing more complicated relationships, are presented here, since in the results for them certain interesting features are evident that are present in only a limited degree in the other cases.

The experimentally determined solubility values are the concentrations in the water phase in equilibrium with the liquid solute phase, saturated with water. Inspection of these values shows but little correlation to exist among them in any of the series of compounds. However, when those energy terms involved in separating the solute molecules from their liquid phase are eliminated, regularities become evident at once. This may be done by recomputing the observed solubilities to vapor solubilities corresponding to a constant standard state of 100 mm. in the vapor. To compute these standard vapor solubilities from the observed solubility values and the vapor pressures of the organic liquids, Henry's law is employed. Except in a few cases (3) this law has not been commonly applied to such systems. While there seems little reason to doubt its validity in the case of dilute solutions, it was deemed better to determine

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this experimentally for systems of the type under consideration here (8). This test showed that it could be used as a first approximation up to concentrations of approximately 400 to 500 millimoles per 1000 g. of water.

The ketones which have been measured are the following: methyl propyl; methyl isopropyl; diethyl; methyl butyl; methyl isobutyl; di-propyl; and dibutyl. All have practically the same dipole moment, 2.7×10^{-18} E. S. U. (10), and by this criterion should have the same polarity. The polarity is due to the large dipole in the carbonyl group, and it is practically unaffected by differences in length or branching of the hydrocarbon side chains. In order to calculate these vapor solubilities and obtain the molecular volumes it was necessary to have data for the vapor pressures and densities of the compounds. In those cases where these values were not available in the literature they were determined for this investigation. The vapor pressure and density data have already been published (7).

EXPERIMENTAL

The saturated solutions of the substances investigated were prepared in each case by shaking an excess of the liquid with water in thin-walled cylindrical glass-stoppered bottles in large water thermostats maintained at 0°, 10°, 30°, 50°, and 75°C. These solutions were analyzed by means of a Zeiss combination liquid and gas interferometer. The method has been described elsewhere in detail (5).

The dibutyl ketone was prepared in this laboratory. All the other substances were of the best grades commercially available. They were purified by methods previously described. Data for the boiling points of five of the compounds have already been published (7). The samples of the remaining two ketones had the following boiling ranges: methyl *n*-propyl ketone, 101.92°–101.94°C.; methyl *n*-butyl ketone, 127.1°–127.2°C. Timmermans (9) gives boiling points of 102.0°C. for methyl propyl ketone and 127.2°C. for methyl butyl ketone.

RESULTS

The solubilities found for the ketones are given in table 1. These observed values were converted to vapor solubilities. The vapor solubility, C_v , is defined as the concentration in the water which would be in equilibrium with the vapor of the substance under a standard pressure p_s of 100 mm. at the temperature in question. If C is the observed solubility and p_L the vapor pressure of the liquid solute at the same temperature, then if Henry's law holds

$$C_v = p_s/p_L \times C$$

In table 2 the values of p_L used are listed and the values of the vapor solubilities determined from them. For later reference there are also

TABLE 1
Solubility in moles per 1000 g. of water

COMPOUND	AT 0°C.	AT 10°C.	AT 30°C.	AT 50°C.	AT 75°C.
	moles	moles	moles	moles	moles
Methyl <i>n</i> -propyl ketone .		0.887	0.630	0.515	
Methyl isopropyl ketone . .		0.813	0.608	0.594	
Diethyl ketone		0.781	0.576	0.456	
Methyl <i>n</i> -butyl ketone .		0.204	0.145	0.124	
Methyl isobutyl ketone . .	0.307	0.231	0.166	0.141	0.137
Dipropyl ketone	0.0643	0.0466	0.0335	0.0288	0.0272
Dibutyl ketone		0.00357	0.00255	0.00243	

TABLE 2
Vapor solubilities and molecular volumes

KETONE	<i>t</i>	<i>C_s</i>	<i>N</i>	Δ_4^{40}	<i>V_m</i>	<i>p_L</i>
	°C.	molarity				mm.
Methyl propyl	10	4.90	0.0812	0.8169	105.4	18.1
	30	1.28	0.0225	0.7984	107.9	49.4
	50	0.432	0.00772	0.7800	110.4	119.1
Methyl isopropyl	10	3.20	0.0545	0.8239	104.5	25.4
	30	0.895	0.0159	0.8052	107.0	67.9
	50	0.370	0.00662	0.7847	109.7	160.6
Diethyl	10	4.68	0.0778	0.8243	104.5	16.7
	30	1.23	0.0217	0.8045	107.0	47.0
	50	0.393	0.00703	0.7867	109.5	116.0
Methyl butyl	10	4.00	0.0673	0.8198	122.1	5.1
	30	0.912	0.0162	0.8025	124.7	15.9
	50	0.288	0.00516	0.7845	127.7	43.0
Methyl isobutyl	0	6.14	0.0996	0.8187	122.3	5.0
	10	2.51	0.0433	0.8094	123.7	9.2
	30	0.617	0.0110	0.7922	126.4	26.9
	50	0.204	0.00366	0.7736	129.4	69.2
	75	0.0708	0.00127	0.7520	133.1	193.4
Dipropyl	0	4.12	0.0691	0.8340	136.8	1.6
	10	1.55	0.0272	0.8248	138.3	3.0
	30	0.353	0.00632	0.8081	141.2	9.5
	50	0.113	0.00203	0.7913	144.2	25.5
	75	0.0360	0.000648	0.7702	148.2	75.6
Dibutyl	10	0.235	0.00422	0.8296	171.1	1.5
	30	0.0536	0.000964	0.8147	174.2	4.8
	50	0.0193	0.000348	0.7981	177.9	12.6

listed in this table the mole fraction, N , corresponding to C_s , as well as the densities and molecular volumes, V_m , at each temperature. The densities were taken from our previously published data (7), except in the cases of methyl propyl ketone, diethyl ketone, and dipropyl ketone. Values for the first two of these were taken from International Critical Tables. The densities for dipropyl ketone were obtained by plotting the values listed in Beilstein (1) against temperature. The vapor pressure values, p_L , were taken from our own data (7) in the cases of diethyl, dipropyl, and dibutyl ketones. Values for the two methyl propyl and the two methyl butyl ketones were calculated from the equations given by Mayberry and Aston (6).

HEAT OF SOLUTION

The temperatures covered by the present data are sufficient to permit a calculation of the heat of solution at several temperatures. For the dilute

TABLE 3
Values of ΔF , ΔH , and ΔS for the ketones

KETONE		AT 0°C.	AT 10°C.	AT 30°C.	AT 50°C.	AT 75°C.
Methyl propyl..	ΔF		4.00	5.05	6.07	
	$-\Delta H$		11.21	10.65	10.32	
	$-\Delta S$		53.8	51.8	50.8	
Methyl isopropyl. . .	ΔF		4.22	5.26	6.17	
	$-\Delta H$		11.48	9.44	8.28	
	$-\Delta S$		55.4	48.5	44.7	
Diethyl.	ΔF		4.02	5.08	6.13	
	$-\Delta H$		10.95	10.95	10.95	
	$-\Delta S$		53.0	52.9	52.9	
Methyl butyl.....	ΔF		4.11	5.25	6.33	
	$-\Delta H$		12.73	11.68	10.40	
	$-\Delta S$		59.4	55.8	51.8	
Methyl isobutyl . . .	ΔF	3.75	4.35	5.49	6.55	7.79
	$-\Delta H$	12.79	12.23	11.14	9.98	9.01
	$-\Delta S$	60.6	58.6	54.9	51.2	48.3
Dipropyl.	ΔF	3.95	4.62	5.82	7.20	8.26
	$-\Delta H$	13.84	13.39	11.52	10.74	10.10
	$-\Delta S$	65.1	63.6	57.2	55.5	52.7
Dibutyl.	ΔF		5.66	6.95	8.06	
	$-\Delta H$		11.87	11.12	10.52	
	$-\Delta S$		61.9	59.6	57.5	

solutions under consideration the heat of solution, ΔH , is given by the relation

$$\ln N = \frac{\Delta H}{RT} + \text{constant}$$

From a large-scale plot of $\log N$ against $1/T$, values of ΔH were determined graphically from the slope at the temperatures listed in table 3. These values, which have also been called the energies of hydration, decrease with increasing temperature, as would be expected. While increasing side chain length up to the dipropyl compound results in increased values of ΔH , the two long side chains in dibutyl ketone operate to decrease the heat of hydration. A possible explanation of this would be that the longer chains may tend to coil back toward the carbonyl group, owing either to the large dipole field around it or to their thermal motion. If this coiling exists it will tend to exclude water molecules from the carbonyl dipole and will also reduce the chances for attractive interaction between the CH_2 groups and the solvent molecules. In agreement with the results of Butler, a decrease in the heat of hydration is observed on passing from the normal propyl or normal butyl ketone to the corresponding iso compounds. The branched side chain would result in an increase in the distance of one of the carbon atoms from the water molecules and thus reduce the magnitude of the London attractive forces. This would be reflected in a decrease in the heat of hydration. The indications for this will be discussed later in connection with the volume relationships.

FREE ENERGIES OF HYDRATION

These have been defined by Butler (3) by the relation

$$\Delta F = RT \ln \frac{p}{\bar{N}}$$

ΔF is the free energy change involved in the transfer of a mole of vapor from the vapor state, where the pressure is p , to the dilute solution where the mole fraction is N . Our choice of the pressure value for the standard state in the vapor is 100 mm. at each temperature instead of the value (1 mm.) used by Butler. This was done because it seemed probable that conversion of the observed values to vapor solubilities, C_s , would involve less error through possible deviations from Henry's law, in view of the number of larger values for p_L involved in our data. This must, however, remain a matter of speculation in the absence of more data. If the form of Henry's law for mole fractions, namely $P/N = \text{constant}$, were assumed valid, no difference in the values of ΔF would result. We have, however, assumed the molality form of Henry's law, $p/m = k$, on the basis of our earlier test. This results in a slightly different value for the mole fraction, N , corresponding to the standard vapor state with 100 mm. pressure, and so causes a slightly different value of ΔF than would be calculated using the

mole fraction form of the law. In any case the difference is small and probably not significant in view of the other assumptions. Thus for the largest observed solubility, that of methyl isopropyl ketone at 10°C., our calculation gives a value of $\Delta F = 4.00$ kg-cal., whereas the mole fraction form of the law gives 3.96 kg-cal. For the majority of our results, which are for much more dilute solutions, no appreciable difference would result. The ΔF values in table 3 are therefore computed from the relation

$$\Delta F = RT \ln \frac{100}{N}$$

where N is the mole fraction corresponding to the value of C_s in table 2.

ENTROPY OF HYDRATION

From the values of ΔH and ΔF given in table 3 the entropy of hydration, ΔS , has been calculated by use of the equation

$$\Delta F = \Delta H - T\Delta S$$

These values are also listed in table 3. Recently Evans and Polanyi (4) have pointed out the existence of simple linear relations between ΔS and ΔH for the solubilities of a solute in a series of solvents, and of relations less generally valid for the solubilities of a series of solutes in a given solvent, the validity in the latter case being limited to solutes which are chemically related. Our data come under the second category. However, in spite of the close similarity in our series of ketones and the fact that they all have the same polarity, as measured by their dipole moments, no linear relation is observed for the group of ketones as a whole. The absence of such a relationship is evident from an inspection of figure 1, in which ΔH is plotted against ΔS for all of the compounds at 10°, 30°, and 50°C. However, in the case of three of the ketones,—methyl propyl, methyl isopropyl, and diethyl,—there is a linear relation which holds well at each of the three temperatures, as the straight lines indicate. Bell (2) has pointed out the existence of a relation between the ΔH and ΔS values for solutions of gases, similar to that found by Evans and Polanyi. In discussing the possible basis of such relations he has stressed the importance of the relative volumes of the solute and solvent. It is significant that this factor is approximately constant in the cases where a linear relation is valid. The molecular volumes of methyl propyl, methyl isopropyl, and diethyl ketones are all approximately the same at the three temperatures. It is possible that this equality of solute volume would be one of the cases discussed by Bell, where it might be legitimate to assume that the configuration of surrounding solvent molecules was disturbed in the same way by each of these closely related solute molecules. In this connection it may be noted that the three solutes, in nitrobenzene as solvent, that Evans and Polanyi (reference 4, table 2) give as an illustra-

tion of a relation between ΔS and ΔH for solutes in the same solvent, would be expected to have approximately the same volume. Whether equality of solute volumes as well as chemical similarity is a prerequisite for the existence of such relations in the case of different solutes in the same solvent can be determined only on the basis of additional data.

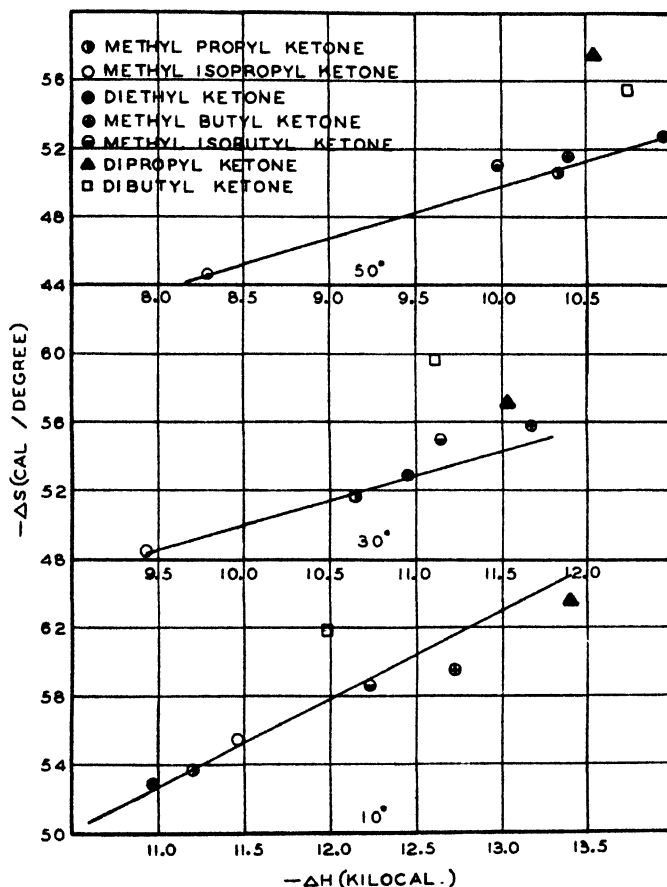


FIG. 1. Relation between heats and entropies of solutions at 10°, 30°, and 50°C.

Obviously this is not essential in the case of the data for different gaseous solutes in the same solvent given by Bell.

VOLUME RELATIONS

The molecular volumes of the pure liquids at the same temperatures as the solubility determinations have been used as criteria of the volumes of the different ketones relative to one another. It is appreciated that this can only be a rough measure of the actual volume occupied by the mole-

cules in the water solutions, but it is likely to be relatively correct in the case of a series of closely related compounds. Several features of these solubility results are brought out when the standard vapor solubility N is plotted against the volume in figure 2. In general, as in the case of other series of compounds, the solubilities decrease with increasing molecular size. A striking feature of the results is shown in the cases of methyl butyl ketone and methyl isobutyl ketone. At 10°C. there is a large difference in the solubility, although the two have approximately the same molecular volume. This difference becomes markedly less at 30°C. and still less at 50°C. This effect in the case of the methyl propyl,

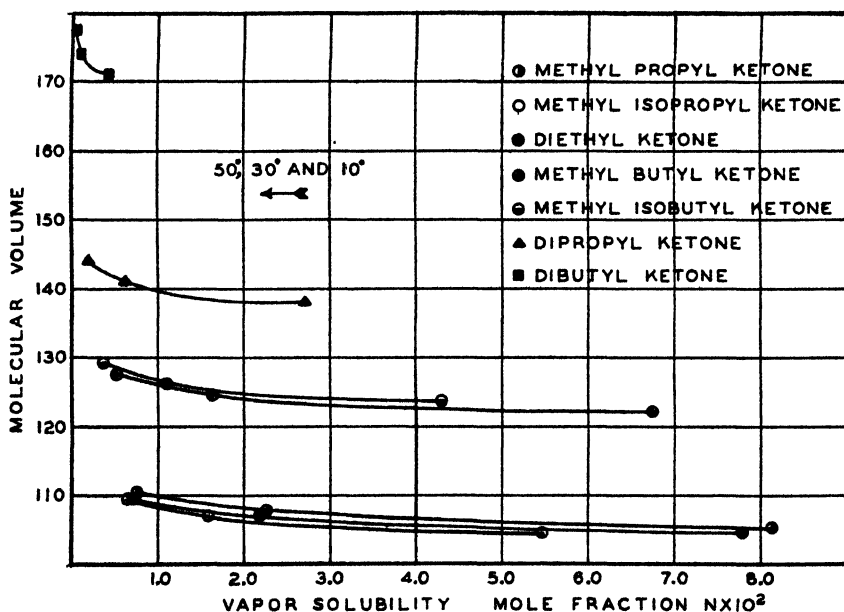


FIG. 2. Effect of temperature on solubilities in relation to volume

diethyl, and methyl isopropyl compounds is even more marked. These have about the same volume at each of the temperatures. At 10°C. methyl propyl ketone is about one and a half times more soluble than methyl isopropyl ketone. This ratio decreases to 1.42 at 30°C., while at 50°C. it drops to 1.16. There is thus a large effect between 10° and 50°C., which is associated with the structural differences in the two molecules. A similar comparison is valid for diethyl ketone and methyl isopropyl ketone.

A possible explanation of these effects would be the following: The methyl isopropyl ketone molecule is a compact branched structure which can assume only a relatively limited number of configurations. It will there-

fore not be much influenced by temperature, nor will this limited number of configurations differ greatly in their positions relative to the surrounding solvent molecules. The two compounds with longer unbranched side chains can assume a larger number of configurations, which will presumably be temperature dependent. Thus, if at low temperatures the side chains are stretched out so that the CH_2 groups are surrounded by the maximum possible number of water molecules, the attractive forces between these groups and water will be large and will add to the main attractive interaction between the carbonyl dipole and the water molecules. If, as the temperature increases, these side chains assume other configurations, these will be such as to decrease the number of water molecules adjacent to the CH_2 groups. The diethyl and normal propyl compounds when in these configurations will have compact structures approaching that of the iso compound. They will have a reduced number of water molecules adjacent to their CH_2 groups, and therefore the magnitude of the attractive forces will decrease.

SUMMARY

The solubilities in water at 10°, 30°, and 50°C. of methyl *n*-propyl, methyl isopropyl, diethyl, methyl *n*-butyl, and dibutyl ketones and those of methyl isobutyl and dipropyl ketones at 0°, 10°, 30°, 50°, and 75°C. have been determined, and vapor solubilities have been computed from them.

Free energies, heats, and entropies of solution for these cases have been calculated. In this series a linear relation between entropies and heats of solution was found only in those cases where molecular volumes were nearly equal.

The significance of the large solubility differences found for isomers and the large temperature dependence of this difference is discussed.

REFERENCES

- (1) BEILSTEIN, F. K.: *Handbuch der organischen Chemie*, 4th edition, Vol. I, p. 700, Appendix 1, Vol. 1, p. 359. Julius Springer, Berlin.
- (2) BELL: *Trans. Faraday Soc.* **33**, 496 (1937).
- (3) BUTLER: *Trans. Faraday Soc.* **33**, 229 (1937).
- (4) EVANS AND POLANYI: *Trans. Faraday Soc.* **32**, 1333 (1937).
- (5) GROSS AND SAYLOR: *J. Am. Chem. Soc.* **53**, 1747 (1931).
- (6) MAYBERRY AND ASTON: *J. Am. Chem. Soc.* **56**, 2682-3 (1934).
- (7) RINTELEN, SAYLOR, AND GROSS: *J. Am. Chem. Soc.* **59**, 1129 (1937).
- (8) SAYLOR, STUCKY, AND GROSS: *J. Am. Chem. Soc.* **60**, 373 (1938).
- (9) TIMMERMAN: *Bull. soc. chim. Belg.* **30**, 62 (1921).
- (10) WOLF, K. L.: *Z. physik. Chem.* **B2**, 39 (1929).

PRESSURE-VOLUME-TEMPERATURE RELATIONS IN SOLUTIONS. I¹

OBSERVATIONS ON THE BEHAVIOR OF SOLUTIONS OF BENZENE AND SOME OF ITS DERIVATIVES

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INTRODUCTION

In common with other properties of liquids and liquid solutions, the pressure-volume-temperature relations depend on the nature of the constituent molecules and the forces between them. The connection between molecular mechanics and thermodynamics is, however, still so obscure in this field that an experimental attack with a view to obtaining empirical generalizations seems not only justifiable but even desirable at the present time. The changes in volume which occur when two components are mixed at different temperatures and pressures to form solutions of various concentrations have been assumed to be closely connected with the intermolecular forces between the components and, moreover, they are quantities of considerable thermodynamic interest because the changes of activity coefficients with pressure may be computed directly from them. In the course of a systematic study of the volume changes on mixing of aqueous solutions at different pressures and temperatures, it became evident that the complex behavior there encountered could be better understood if more were known about the behavior of simple solutions. Binary mixtures of benzene and some of its monosubstituted derivatives appeared to be suitable for such an investigation. Many of their properties have been investigated, the densities, vapor pressures, and dielectric constants, quite recently, in fact (11, 12); it is highly unlikely that structural effects complicate the behavior of these solutions.

This paper presents a few questions of more general interest which have arisen during a systematic study of the densities, compressions, and thermal expansions of mixtures including benzene, aniline, chlorobenzene,

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bromobenzene, and nitrobenzene. The complete results will be published elsewhere.

COMPRESSIONS OF THE PURE COMPONENTS

The compressions of the liquid components (suitably purified) to 500 and 1000 bars (metric atmospheres) were measured at 25°, 45°, 65°, and 85°C. in our latest pressure apparatus (4). We had already found (6) that the bulk compressions of benzene were represented within experimental error by the Tait equation:

$$k = C \log [(B + P)/B] \quad (1)$$

where k is the bulk compression and P the pressure; B and C are constants, the latter being independent of the temperature.

TABLE 1

Constants in the Tait equation for benzene and some of its derivatives at different temperatures

For all the liquids at all temperatures $C = 0.21591$

SUBSTANCE	ν AT 25°C.	B IN KILOBARS			
		25°C.	45°C.	65°C.	85°C.
Benzene	1.14461	0.970	0.829	0.701	
Chlorobenzene	0.90817	1.248	1.0978	0.9609	
Bromobenzene	0.67177	1.4044	1.2473	1.1033	
Nitrobenzene	0.83451	1.8652	1.6794	1.5035	
Aniline	0.98291	2.009	1.7983	1.6056	1.4304

Using the same value of C as we had employed for benzene, we were able to calculate B for the other liquids from the compressions at 1000 bars. These values of C and B , when used in equation 1, reproduced our determinations at 500 bars within experimental error, and we have found by repeated checks at intermediate pressures that this agreement at 500 bars means that the equation reproduces the compressions to any pressure between 1 and 1250 bars.

In table 1 we give the value of the constant C and the values of B (in kilobars) at different temperatures, the figures for benzene being taken from the previous paper. The fact that C is independent of temperature and the same for all these liquids supports the suggestion made by Dr. Teller (private communication) that it depends on the repulsive forces between the molecules themselves.

It follows from the constancy of C that the compressibility of any of the monosubstituted derivatives of benzene mentioned in table 1 is the same as that of benzene itself under a hydrostatic pressure equal to the difference between the net internal pressure (B) of the compound and that of benzene.

In other words, the introduction of a polar group acts on the compressibility of benzene in the same way as the application of an external pressure,—it changes the attractive potential but leaves the form of the repulsive potential unaltered. From an analysis of the results for benzene it has been shown (6) that B may be interpreted as the difference between the cohesive pressure set up by the attractive forces between the molecules and the expansive pressure due to the thermal energy of the molecules, ($RT/(V - b)$ in van der Waals' equation). In other words, B represents the *net internal pressure* of the liquid. Increase in the attractive potential between the molecules, decrease of temperature, and increase in the free volume ($V - b$) all cause B to increase in value. There is a rough parallelism between B and the electric moments of the molecules in the dif-

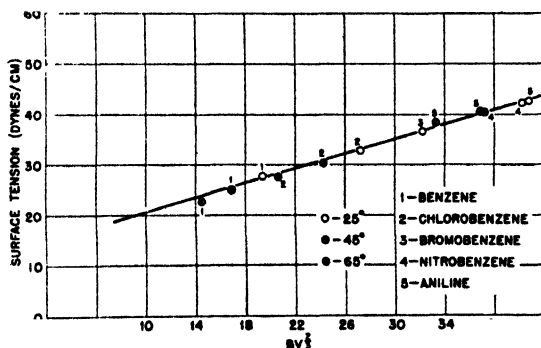


FIG. 1. The surface tensions of benzene and some derivatives at different temperatures plotted against the average force between the molecules (in 10^9 dynes per mole) computed on the assumption that B is the net internal pressure.

ferent liquids, but the parallelism is so rough that we must conclude that the dipole forces do not play a predominating rôle in determining B .

The surface tensions of these liquids at different temperatures are closely related to their net internal pressures. In figure 1 we have plotted the surface tensions (interpolated from the data given in the Landolt-Börnstein Tables) of the various liquids at 25°, 45°, and 65°C. against $BV^{1/3}$, a quantity which represents the average force acting on one mole of a liquid whose net internal pressure is given by B . The points for all five compounds at 25°C. lie on a straight line, and the points for the higher temperatures scatter very closely around this line. As the surfaces of all these liquids are presumably the same as that of benzene, we should expect the surface tension to be determined almost completely by the intermolecular forces and the size of the molecules. Figure 1 may be taken as contributory evidence in favor of our interpretation of B .

By means of the Tait equation we may compute the molal volumes of

benzene under hydrostatic pressures at which its compressibility is equal to that of its derivatives. On comparing molal volumes under such conditions (constant B) we obtain very reasonable estimates of the volumes of the substituent groups. It will be seen from the foregoing that this is equivalent to a comparison of parachors (15).

Relations between surface energy, compressibility, internal pressure, etc. have been studied extensively for many years (2, 8). We seek to avoid confusion by emphasizing that the *net internal pressure* B is not equal to the internal pressure defined in any of the usual ways (8) such as $(\partial E/\partial V)_T$.

APPARENT VOLUMES, EXPANSIONS AND COMPRESSIONS OF ANILINE IN SOME SOLUTIONS

The specific volumes of solutions of aniline in benzene, chlorobenzene, and nitrobenzene were measured at 10°C. intervals between 25° and 75°C. in a new weight-dilatometer made of fused silica. The compressions to 500 and 1000 bars of the same solutions were also determined over this temperature range. From these data the apparent volumes of aniline in the different solutions were computed at various pressures and temperatures. It will be recalled that the apparent volume (per gram) of a component in a binary mixture is defined by the equation:²

$$v = x_1 v_1^0 + x_2 \phi_2$$

and it may be noted that the volume change taking place when the requisite amounts of components are mixed to form 1 g. of solution is given by

$$x_2(\phi_2 - v_2^0) \quad \text{or} \quad x_1(\phi_1 - v_1^0)$$

In figure 2 we have plotted $(\phi_2 - v_2^0)$ in milliliters per gram for aniline in different solvents at various concentrations, pressures, and temperatures against the mole fraction of aniline. It will be noted that a wide variety of behavior is represented on this diagram. Benzene and aniline contract on mixing; this contraction increases with temperature and diminishes with pressure. Aniline and chlorobenzene expand slightly on mixing; the expansion is almost independent of temperature and is increased by rise of pressure. A greater expansion is observed on mixing aniline and nitrobenzene, but this expansion diminishes with pressure. Our compressibility results are given in more detail in table 2, where observed values of B are

² The symbols used in this paper are as follows: The subscripts 1 and 2 refer respectively to each component in the solution; generally aniline is taken as component 2. The weight fraction is represented by x , the mole fraction by X , the specific volume of the solution by v , the molal volume by V , the apparent volume by ϕ , and the relative volume change with pressure (bulk compression) by k . The superscript 0 denotes the pure liquid component. Δ_P indicates the finite change with pressure of the quantity to which it is prefixed. P is the pressure; T is the absolute temperature.

recorded, and in figure 3, where the differences between the apparent compressions to 1000 bars of aniline in solution and of pure aniline are plotted against the mole fractions of aniline in different solutions. Compressions of the solutions to 500 bars confirmed the presumption that the constant C was the same for the solutions as for the pure liquids. It will

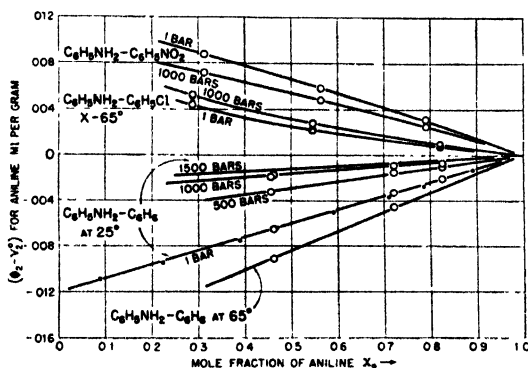


FIG. 2. The difference between the specific volume of aniline and its apparent volume in different solvents at various temperatures, pressures, and concentrations. The black dots represent results computed from the data of Martin and Collie.

TABLE 2

Constants in the Tait equations for the compressions of solutions at 25°C.

In all cases $C' = 0.21591$

SOLUTION	WEIGHT FRACTION OF ANILINE	VOLUME FRACTION OF ANILINE	B' IN KILOBARS
Aniline-benzene	0.8507	0.8303	1.7887
	0.7560	0.7268	1.6693
	0.5050	0.4669	1.3838
Aniline-chlorobenzene	0.7923	0.8050	1.8210
	0.4995	0.5192	1.5857
	0.2482	0.2632	1.4080
Aniline-nitrobenzene	0.7410	0.7712	1.9506
	0.4952	0.5360	1.9132
	0.2536	0.2875	1.8832

be seen from figure 3 that the compressions of aniline-benzene and aniline-chlorobenzene mixtures are less than those computed from the simple law of mixtures, whereas in aniline-nitrobenzene solutions the opposite holds.

NET INTERNAL PRESSURES AND VOLUME CHANGES ON MIXING

In dealing with solutions whose components differ widely in compressibility, such as aqueous salt solutions, we have applied Tammann's

hypothesis that the solvent (component of the greater compressibility) in the solution behaves as if it were under an external hydrostatic pressure, and we have shown that the volume changes on mixing may be computed with useful accuracy from the observed compressions or net internal pressures (3, 5). The method involves one assumption concerning the compression of the solute, however, which makes it inadequate for solutions whose components do not differ widely in compressibility, such as those we are now discussing, but it can readily be modified. In view of the fact that the constant C in the Tait equation is the same for all the liquids and solutions mentioned here, we may apply the following argument: Let B_1 , B_2 , and B' be the net internal pressures of the pure components and of the solutions, respectively. When the net internal pressure of a component is

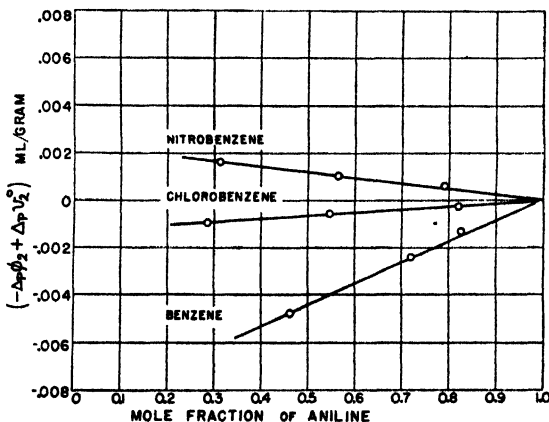


FIG. 3. The difference between the specific compression of aniline and its apparent compression in different solutions. The pressure range is 1 to 1000 bars.

changed from B_1 to B' , the corresponding volume change according to the Tait equation is given by equation 2:

$$-\Delta_F v_1 = v_1^0 C \log \frac{B'}{B_1} \quad (2)$$

If we assume that, on forming the solution, the components first expand until their net internal pressures come to the common value B' and then mix without further change, we arrive at the following formula:

$$\frac{-\Delta v}{C} = (x_1 v_1^0 + x_2 v_2^0) \log B' - (x_1 v_1^0 \log B_1 + x_2 v_2^0 \log B_2) \quad (3)$$

In this equation $-\Delta v$ is the decrease in volume when 1 g. of solution is made from the appropriate quantities of the pure components. It should be noted that C is independent of temperature etc. only when the com-

pression is expressed as the volume change per unit volume, and this constancy of C leads to a relation involving $\log B'$ and the *volume fractions* of the components. In view of the increasing importance that is being attached to the volume fraction by theoretical workers (7, 14), we regard this observation as significant.

In figure 4 we have plotted $\log B'$ against the volume fractions of aniline,

$$\left(\frac{x_2 v_2^0}{x_1 v_1^0 + x_2 v_2^0} \right)$$

in the three series of solutions (open circles). Qualitatively the formula holds; where $\log B'$ falls below the straight lines joining $\log B_1$ and $\log B_2$, the volume change on mixing is positive, and where the points for $\log B'$

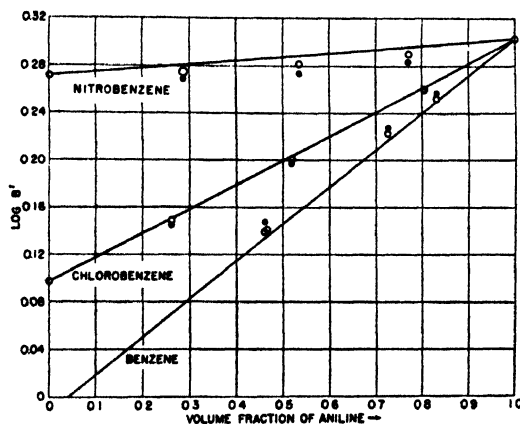


FIG. 4. Illustration of the relation between the logarithm of the net internal pressure of solutions of aniline at 25°C. and the volume fraction of the components. The open circles indicate the observed values of $\log B'$, and the dots, the values computed from the volume change on mixing.

fall above this line, the volume change on mixing is negative. Quantitatively equation 3 leaves something to be desired. The black dots in figure 4 represent values of $\log B'$ computed from the observed volume changes on mixing. The agreement gets progressively worse as the solutions become more dilute in aniline, except in the case of nitrobenzene. This may be due in part to our overstraining the Tait equation by using it to extrapolate to negative pressures exceeding 500 bars. The volume changes on mixing computed from the observed values of B agree with those actually measured within a factor of 2, and, as these volume changes are very small as compared with the specific volumes of the components, we may say that the agreement is not despicable.

Solutions of aniline and nitrobenzene were chosen for examination

because the net internal pressures of the pure liquids were nearly the same and hence less extrapolation with the Tait equation was necessary. The agreement between the observed and calculated values of $\log B'$ is, however, particularly poor for these solutions, a fact for which another phenomenon to be discussed later must be held partly responsible. Summing up, we may say that equation 3 gives a means of calculating approximately the compressibilities of a solution from the volume changes on mixing, or *vice versa*, provided that the volumes and the net internal pressures of the components are known. It gives a means of connecting the volume change on mixing with the net internal pressure of the solution.

Figure 5, giving the results of computations from Bramley's data (1), shows that the volume changes occurring when phenol is dissolved in various solvents parallel those we have observed with aniline. We are,

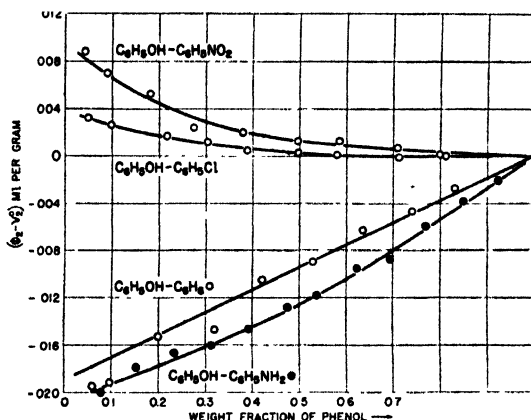


FIG. 5. The difference between the specific volume of phenol and its apparent volume in different series of solutions, as computed from Bramley's data.

therefore, not dealing with any isolated case. An essential feature of figures 2, 4, and 5 is that, as the ratio of the net internal pressures of the pure components approaches unity, the volume change on mixing per unit of aniline or phenol becomes more positive, and accordingly the departures of $\log B'$ from the straight lines become more negative. This statement covers not only the volume changes at 25°C. but also the results at different pressures and temperatures. From table 1 it will be seen that the ratio of the net internal pressures for aniline and benzene approaches unity as the temperature falls; for aniline-chlorobenzene solutions this ratio changes in the same direction but to a much less extent. At higher pressures the quantity $(B + P)$ must be used instead of B , and it is obvious that the higher P is, the closer will the ratios of $(B + P)$ for pairs of the liquids approach unity. Figure 6 shows that at 1000 bars (1 kilobar) the depar-

tures of $\log (B' + P)$ from the straight lines are more negative than at atmospheric pressure. Our investigations of aqueous and non-aqueous solutions of electrolytes have led us to similar conclusions about the relations between the volume changes on mixing and the ratio of the compressibilities of the components in those cases where structural effects do not predominate (5).

The activity coefficients of aniline, phenol, nitrobenzene, chlorobenzene, etc. in benzene solutions all increase as the solutions become more dilute, and the activity coefficients have been adequately correlated with the change in electrostatic energy of the solutions arising from changing concentrations of the polar molecules (11). Negative values of $(\phi_2 - v_2^0)$ mean that the activity coefficients decrease with pressure and that the chemical potential of the solute becomes closer to what it would be in the

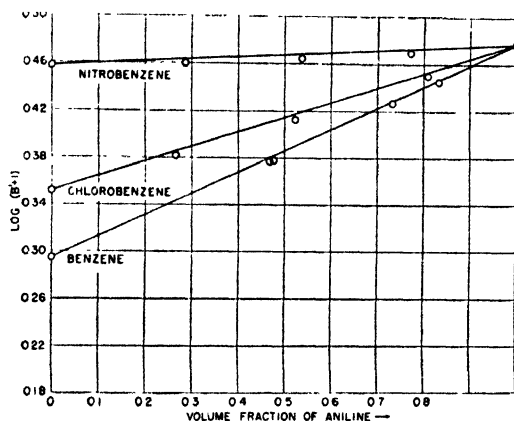


FIG. 6. The logarithms of the net internal pressures of aniline solutions at 25°C. and 1000 bars plotted against the volume fraction of aniline.

ideal solution of the same chemical nature as the pure solute. In other words, the electrostatic energy due to the polar molecules becomes relatively less important as the volumes of the solutions are diminished, short-range forces becoming quite significant.

NITROBENZENE-ANILINE MIXTURES

What has been said in the preceding discussion is applicable to nitrobenzene-aniline solutions except that rise of pressure appears to decrease rather than increase the change in volume on mixing. These solutions present a rather interesting phenomenon. It has been known for a long time that when reasonably pure nitrobenzene and aniline are mixed, the solution instantly develops a deep orange color (10, 13). Investigation of the thermodynamic properties and viscosities of these solutions (10, 16)

has revealed no trace of compound formation in the usual sense of the term. It occurred to us that a grouping of the aniline molecules around the highly polarizable nitro group, the energy of association being quite low, might account for this color, and, if so, the absorption of light should be pushed even farther towards the red by application of hydrostatic pressure. Such was found to be the case. With a suitable blue light-filter, a reversible color change from green to yellow could readily be seen as the pressure over the solution was raised. This phenomenon is now being systematically studied, and further details will be published later. It is mentioned here to show that nitrobenzene-aniline solutions exhibit a curious type of intermolecular phenomenon, but further speculations about the effect of pressure on these solutions must wait till the phenomenon is more carefully investigated.

We must state in conclusion that we still regard the theoretical implications of the Tait equation as very obscure. Similar equations on a much sounder theoretical basis have been developed (9), but they lack the simplicity of the Tait equation. It is our purpose to apply this equation empirically until it breaks down completely; in so doing we hope to uncover what is most needed at present in the study of liquids, some valid simplifying assumptions.

SUMMARY

New measurements of the compressions and expansions of some derivatives of benzene and of the specific volumes, compressions, and expansions of mixtures of benzene and these derivatives have confirmed and extended the empirical use of the Tait equation. The exponential constant C in this equation has been found to be the same for all the liquids and solutions examined, and the internal pressure constants, B , for the pure liquids and the solutions have been correlated with volume changes which take place when the liquids are mixed. The conclusions based on studies of electrolytic solutions concerning the volume changes on mixing and the internal pressures of the components are found to hold qualitatively in benzene solutions. A new phenomenon in aniline-nitrobenzene solutions is described.

REFERENCES

- (1) BRAMLEY, A.: *J. Chem. Soc.* **109**, 10 (1916).
- (2) EDSEER, E.: *Brit. Assoc. Colloid Repts.* **4**, 40 (1922).
- (3) GIBSON, R. E.: *J. Am. Chem. Soc.* **57**, 284 (1935).
- (4) GIBSON, R. E.: *J. Am. Chem. Soc.* **59**, 1521 (1937).
- (5) GIBSON, R. E.: *Am. J. Sci.*, in press.
- (6) GIBSON, R. E., AND KINCAID, JOHN F.: *J. Am. Chem. Soc.* **60**, 511 (1938).
- (7) GUGGENHEIM, E. A.: *Trans. Faraday Soc.* **33**, 151 (1937).

- (8) HILDEBRAND, J. H.: Solubility, Chap. 9. The Chemical Catalog Co., Inc., New York (1924).
- (9) KINCAID, JOHN F., AND EYRING, H.: J. Chem. Phys. **5**, 593 (1937).
- (10) KREMAN, R.: Monatsh. **25**, 1271 (1904).
- (11) MARTIN, A. R.: Trans. Faraday Soc. **33**, 191 (1937).
- (12) MARTIN, A. R., AND COLLIE, B.: J. Chem. Soc. **1932**, 2658.
- (13) OSTROMISLENSKY, I.: Ber. **44**, 268 (1911).
- (14) SCATCHARD, G.: Chem. Rev. **8**, 321 (1931).
- (15) SUGDEN, S.: J. Chem. Soc. **125**, 1177 (1924).
- (16) TSAKALATOS, D. E.: Bull. soc. chim. [4] **11**, 284 (1912).

ASSOCIATION THROUGH HYDROGEN¹

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Any discussion of association through hydrogen in solution is likely to become involved with the question of the terminology most suitable to characterize the bond. This is relatively an academic question, as compared to the facts of association, but it is always desirable to formulate our ideas, if possible, so that the facts will fit into a consistent picture. Some may wish to say that a postage stamp sticks to an envelope because of simple dipole interaction, but until one specifies more particularly what he means by simple dipole interaction, the question is still open. There are physicists, for example, who have said that there is no such thing as chemical valence, only Coulomb forces between protons and electrons. This is true apparently as an abstract statement, but the attempt to describe a molecule in terms of nothing but Coulomb forces leads to absurd conclusions, and the wave mechanics presents us with a picture so different from the classical one, that it is customary to speak of the "exchange" forces, as though they were an entirely new type of force. The attempt to describe association through hydrogen in terms of simple dipole interaction seems to involve, to a lesser degree perhaps, an oversimplification, similar to that mentioned above. In a contribution to a symposium of the Faraday Society upon the dipole moments some years ago, one of the authors (7) rather ungraciously devoted considerable space to showing that dipole moments were disappointing in their significance to chemistry. For example, in the hydrogen halides the dipole moment decreases (presumably) monotonically with increasing atomic weight, whereas the acid strength behaves in the contrary manner so far as it appears to show any trend.² Simple ionic or dipole pictures here are obviously inadequate. Of course it is only fair to state that the dipole moment as measured is not as a rule the one in which we are interested. One may not measure the

¹ Presented at the Symposium on Intermolecular Action, held at Brown University, Providence, Rhode Island, December 27-29, 1938, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society.

² Another example of a related character is the case of the silver halides, where from considerations of ionic radii one would predict that silver iodide would be more soluble than silver chloride.

dipole moment in a polar solvent, and in the case of polyatomic molecules one measures the vector sum of the moments. When we have methods for estimating the dipole moments associated with particular bonds we have, as we shall see later in this paper, a valuable method for explaining behavior.

As a matter of fact, for most molecules the vector sum of the dipole moments is all that is necessary, since no association due to dipole interaction occurs. It is only when hydrogen is present that one finds a strong tendency toward association, and here one may assume at once that the small size of the atom permits a close approach, which allows a strong interaction to take place between dipoles, for example. But this simple picture is by no means adequate to predict what is observed in the association through hydrogen. According to this simple picture molecules should not form dimers of zero dipole moment, as do the carboxylic acids, and of course one knows that here something much more complicated than a simple dipole attraction is taking place. Again one finds no association taking place between hydrogen chloride molecules, regardless of the considerable dipole moment. Finally, one may anticipate difficulty in correlating any of the properties of the hydrogen halides which involve the hydrogen, just as in the case of the acid strengths cited above. This would certainly appear to be true in regard to the tendency to form hydrogen bonds. One of the most interesting properties of the hydrogen halides is their tendency to form the so-called "onium" compounds. Those formed with ammonia are typical salts, but those formed with ether can scarcely be explained on any other basis than hydrogen bond formation. They exist in solution in a solvent of low dielectric constant and even in the gaseous state (4). The reported absence of dissociation of dry ammonium chloride in the vapor state is doubtful not because, as some have supposed, such a molecule could not exist, but rather because it could not be in equilibrium with the dissociation products. As a matter of fact there is some evidence that this dissociation reaction may be measurably slow in the dry state (8). It is true that solutions of ether and hydrogen chloride show some slight electrical conductivity and *might* be supposed to be otherwise largely dissociated into neutral molecules, but infrared absorption shows evidence of hydrogen bonding. The dipole moment of hydrogen iodide is so small that dipole interaction should be negligible. We have not investigated the other hydrogen halides with the infrared technique, but there is no doubt of their tendency to form compounds with ether and no evidence for any marked difference in their behavior.

In the article referred to above it was shown that the clue to the apparently anomalous behavior of the hydrogen halides lies in the fact that under certain circumstances the binding between hydrogen and halogen might undergo a marked change in character and become nearly or completely ionic. It is not necessary here to discuss at length the fact that

most chemical bonds can be described by a combination of homopolar and ionic wave functions. It is obvious that chemical bonds vary all the way from the strictly non-polar to the ionic type, the dipole moment being a rough measure of the amount of ionic binding, when the bond is between unlike molecules. In simple molecules in an isolated state no bond is of completely ionic type, not excepting the alkali halides. In a medium of high dielectric constant the ionic character is, however, favored by energy considerations. Perhaps the most nearly perfect example of an ionic bond is to be found in the FHF^- ion as it exists in solution or the crystal state. This is perhaps also the most perfect example of hydrogen bonding that we know.

We may, therefore, assume that the formation of a hydrogen bond involves an increase in the ionic character of the bonding. Since these bonds are formed, however, in solutions of low dielectric constant or even in the vapor phase, it becomes important to explain how this comes about and to define the conditions under which it may be expected to happen.

The explanation appears to be as follows: A proton attached to an atom by a pair of electrons may be attracted to a pair of electrons belonging to another atom. As a result of this attraction the proton moves away from the first pair of electrons and the bond becomes ionic in character. This can happen even when the molecules are not in a medium of high dielectric constant.

This was the point of view taken by Latimer and Rodebush (3) in 1920 in their attempt to explain the fact (well recognized even at that time) that the degree of ionization of an acid depends upon the basicity of the solvent. There seems to be no necessity to modify their viewpoint in its essential details. It is true that recent theory does not show the hydrogen atom to be linked to two pairs of electrons in covalent bonds, but the transformation to an ionic character, together with the possibility of resonance, allows us to retain the essential picture unaltered.

We have thus two atoms, one of which acts as donor and one as acceptor of the proton. G. N. Lewis has aptly defined the basicity of an atom as the readiness with which it shares electrons with another atom. We see, therefore, that the more basic the atom, the more readily it acts as acceptor, and of course we should likewise assume that the more acidic the atom to which the hydrogen is linked, the more readily it acts as donor. The dipole moment does not in general give us a direct measure of the acidity of a hydrogen atom in a molecule and, as we shall see later, it is not always easy to predict the tendency toward hydrogen bond formation. If the donor atom is sufficiently acidic and the acceptor atom sufficiently basic a salt is formed as, for example, ammonium chloride, but hydrogen bond formation can always be considered to be an intermediate step, just as it is the initial step in the ionization of an acid.

A negative ion is basic by virtue of its net charge, for example, F^- , where-

as a positive ion can hardly act as a base under any circumstance. If one considers only neutral molecules, however, then the basicity must in general be greater the smaller the dipole moment. This point is illustrated by the molecules ammonia, water, and hydrogen fluoride.

It is interesting to consider the structure of the hydrogen fluoride ion, FHF^- . Pauling has characterized it as ionic and has pointed out that formally it satisfies the condition that the coordination number for the proton is 2. This picture is undoubtedly essentially correct. If we assume, however, that the proton is equally distant from the two fluoride ions we find that the distance between the hydrogen and either fluorine, 1.2 Å., is somewhat less than we should expect for ions but somewhat greater than the distance of 0.92 Å. found for the hydrogen fluoride molecule from the band spectrum. We may, therefore, conclude that the hydrogen fluoride ion involves both structures



with quantum mechanical resonance between them. The final result is a structure that is essentially ionic in character.

So far as the authors are aware no hydrogen bond exists without a proton lying somewhere intermediate between two pairs of electrons. The existence of a free pair of electrons held by a somewhat basic atom appears to be the essential condition for association of a molecule with the hydrogen of another molecule. It is the interaction with the pair of electrons that pulls the proton away from the pair of electrons to which it was originally attached and brings about the increase in the ionic character of the bond.

INFRARED SPECTROSCOPY AS A METHOD OF DETERMINING THE EXISTENCE OF HYDROGEN BONDS

Chemists, above all other scientists, know the value of experimental data as compared with speculation. If we can find under what conditions association through hydrogen takes place we shall be in a much better position to discuss the mechanism. While an enormous amount of chemical data points overwhelmingly toward this type of association, as we shall mention later, the method *par excellence* for the discovery of hydrogen bonding is that of infrared spectroscopy. It is not the place here to discuss the method in detail, but credit must be given to Wulf and his collaborators for discovery of its usefulness (1). The particular utility of the method of infrared spectroscopy lies in the fact that the vibrational frequency of hydrogen in a molecule is, because of the small mass of the hydrogen, nearly independent of the rest of the molecule. In table 1 is given the frequency in wave numbers for a number of molecules containing hydrogen. This frequency is the one which involves as a rule the stretching of the covalent bond by which the hydrogen atom is linked to the rest of the

molecule. In another column are indicated the relative intensities of absorption. Only the relative order of magnitude of intensity is given. It is not possible to determine molal absorption coefficients once and for all, because these vary with various factors, including resolving power and total concentration.

The frequencies (table 1) are for the substances in dilute carbon tetrachloride solution. It has been found that these frequencies are only slightly different from those for the same molecules in the vapor state, so that one may assume them to be entirely comparable. The advantages of working in solution are obvious, and for the study of association a solution is of course necessary.

Several comments may be noted in regard to the data of table 1. For example, judged by the vibrational frequency the O—H bond is stronger than the C—H bond, yet the hydrogen of the O—H bond is much more

TABLE 1
Infrared absorption of hydrogen in various molecules

MOLECULE	FREQUENCY	INTENSITY
	<i>cm.⁻¹</i>	
ROH	3640	Strong
RCOOH	3550	Strong
RCOOD	2680	Strong
CCl ₃ COOH	3520	Strong
R ₂ NH	3460	Medium
RCONHR	3450	Medium
C—H (aliphatic)	ca. 2990	Weak
C—H (aromatic)	3075	Weak
CHCl ₃	3050	Weak

active. This activity involves the ionization of the hydrogen, so that one may say that in the case of hydroxyl the ionic type of bonding is favored because of the high effective nuclear charge of the oxygen atom. Even if the carbon-hydrogen linkage were transformed to the ionic type there would be little tendency toward dissociation because of the (presumably) small ionic radius of the carbon, but one may suppose that the ionic type of binding has a much higher energy in the C—H bond than the homopolar type. As an interesting comparison one may say that the dipole moment of the C—H link is probably nearly as great as that of hydrogen iodide, but the latter linkage transforms much more readily to the ionic type.

If we consider the frequency of the hydroxyl in various molecules we see that these vary from 3700 cm.^{-1} for the alcohols to 3500 cm.^{-1} for trichloroacetic acid. It is evident that here the change in frequency is a

measure of the acidity of the hydrogen. This variation in frequency appears to be entirely at variance with that noted in comparing the C—H and O—H frequencies. Actually, however, if one assumes again that it is a measure of the decreasing strength of the homopolar bond, then it accounts for the greater tendency toward the ionic type of bonding that must accompany increasing acidity.

On the other hand, the intensity factor must depend upon the amount of ionic binding present. The absorption coefficient depends upon the change in the dipole moment with the change in internuclear distance, but this in turn varies as a rule with the absolute magnitude of the moment, so that it follows that the intensity increases markedly from C—H to O—H.

In table 2 are listed the observed frequencies of the hydrogen for a number of molecules under conditions where association with the formation of a hydrogen bond is believed to take place. In general it will be

TABLE 2
Shift in frequency upon formation of a hydrogen bond

MOLECULE	ORIGINAL FREQUENCY	BONDED FREQUENCY
	cm. ⁻¹	
ROH.....	3640	3330
RCOOH.....	3550	3000-2670
RCOOD.....	2680	2240
RCONHR.....	3450	3330-3100
HCl.....	2850	2415
CHCl ₃	3050	2970
MOLECULE	BENDING FREQUENCIES	
HOH....	1610	1640
CHCl ₃	2410	2440

noted that there is a marked shift toward longer wave length, the amount of the shift depending upon the activity of the hydrogen (10). In those cases where the shift is large the absorption band is usually broad, showing, in the case of the carboxylic acid complex, considerable structure. Furthermore, there is in every case a marked increase in intensity of absorption.

It seems clear that we have here a method of great sensitivity and reliability, since, in every case that we have tried, where there is any reason to expect association, we have observed this shift in frequency. This lowering of frequency is easily accounted for. The proton attached to a pair of electrons on one atom is attracted to another pair of electrons on an adjacent atom. These opposed attractions result in a reduction of the effective force constant with a considerable lowering of the frequency of vibration.

Even more significant, perhaps, is the marked increase in the intensity of the absorption. The increase in the ionic character of the binding upon the formation of a hydrogen bond must involve an increase in the separation of the proton from the atom to which it was originally attached and an increase in the dipole moment. The significant thing for absorption intensity, however, is the ratio of the change in dipole moment to the change in distance, and the increase in ionic character of the binding must result in an increase in this coefficient.

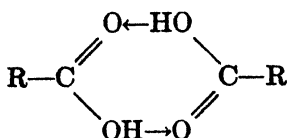
The foregoing considerations apply to the stretching frequency. The bending frequency, which is also infrared-active but of course much less in magnitude, should be increased, since the formation of a hydrogen bond introduces an additional constraint upon the lateral movement of the proton. The frequency observed at 2400 cm.^{-1} in the case of chloroform is, we believe, the first overtone of the bending frequency of the hydrogen, and it shows a marked increase in frequency when a chloroform-quinoline complex is formed. Another case of the increase in the bending frequency upon the formation of a hydrogen bond has been observed by Dr. R. C. Gore of this laboratory. The bending frequency of the water molecule in the vapor state is known to be 1596 cm.^{-1} . The frequency (6) in the liquid state because of hydrogen bonding is increased to 1630 cm.^{-1} , in contrast to the usual situation where the frequencies of a molecule in the liquid state are slightly greater than for the same molecule in the vapor state.

One may tabulate the results of infrared study of hydrogen bonding as follows:

MODE OF VIBRATION OF HYDROGEN		FREQUENCY	INTENSITY
Stretching Vibration	First overtone	Decreased	Disappears
	Fundamental		Increased
Bending Vibration	First overtone	Increased	Increased
	Fundamental	Increased	Increased

RESONANCE IN STRUCTURES INVOLVING HYDROGEN BONDS

The probability that resonance occurs in the hydrofluoride ion has already been mentioned. In the case of the carboxylic acid we have a particularly interesting behavior. A dimer is formed which has zero dipole moment and a complex infrared absorption pattern. Pauling (6) has shown by electron diffraction that an eight-membered ring is formed, the structure of which is quite symmetrical except for the hydrogens.



It is obvious now that the hydrogens will exchange position in the respective molecules, moving simultaneously in opposite directions as indicated by the arrows. This oscillation frequency is not very high, but it can be calculated presumably from the doublet separation observed in the infra-red spectrum, which is of the order of magnitude of 10 to 20 cm^{-1} .

If now we replace the hydroxyl group in the acids by an amino group, giving an acid amide, we may predict an interesting structure.

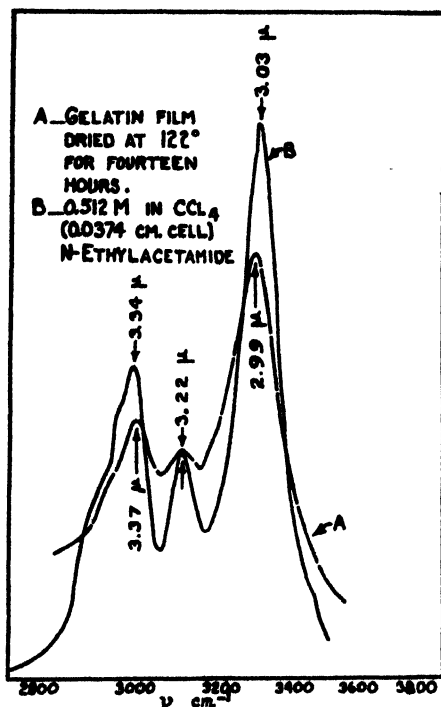
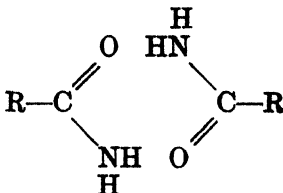


FIG. 1. Comparison of absorption spectra of gelatin and *N*-ethylacetamide

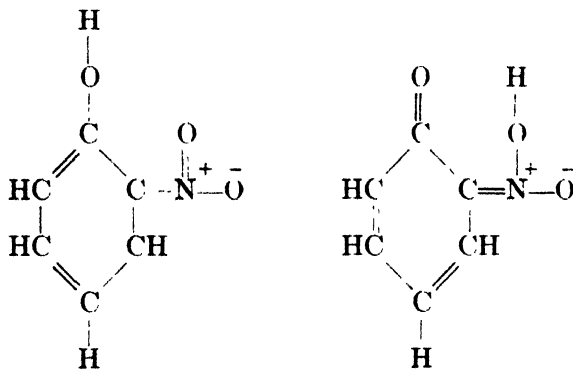
The transfer of the hydrogens would now result in what we might term a reciprocal enolization. Since we would now have hydroxyl instead of amino groups, we should no longer expect an oscillation, as one form might well be much more stable than the other. This reciprocal enolization is

actually observed in the case of the monosubstituted amide



Here we find a strong absorption at $3.0\ \mu$, characteristic of a hydrogen-bonded hydroxyl and very little absorption due to the N—H bond. However, the absorption spectrum is entirely unlike that of the carboxylic acids, so that one cannot be sure of the correctness of the hypothesis of a dimer.

As a matter of fact there is some evidence from freezing point data in favor of a trimeric formula for the amides. Furthermore, the amide molecule shown above is almost identical in structure with the peptide link in the proteins. A comparison of the absorption spectrum of the associated amide with that of gelatin shows a striking resemblance (see figure 1). It is, perhaps, of considerable significance that the trimeric formula for the associated amide bears a strong resemblance to the ring of Wrinch's theory of protein structure (11). Another case wherein resonance is probably significant in the formation of a hydrogen bond is found in the case of the chelated compounds. For example, *o*-nitrophenol may be written with two structures, differing primarily in the point of attachment of the hydrogen



These compounds show the strong absorption in the 3.0 region, which is characteristic of hydrogen bonding, just as do intermolecular compounds.

In the discussion just preceding we have been concerned with molecules which are capable of undergoing keto-enol transformation. This is a phenomenon of great importance in organic chemistry. It has been recognized for a long time that the ketonic and enolic forms are tautomers and that the relative amounts of the two forms are greatly influenced by the solvent. From our studies upon the phenomenon by means of infra-red spectroscopy we have concluded that the enolization of molecules always involves hydrogen bond formation.

ASSOCIATION A UNIVERSAL PHENOMENON

The most striking result of the study of association through hydrogen by means of the infrared technique is that it appears to be a universal phenomenon. Thus, not only are polar liquids such as water completely associated through hydrogen bonds (containing no unbonded or "free" hydroxyl), but glucose, starch, and proteins are also. Likewise, while it has long been known that carboxylic acids are associated to a high degree in inert solvents, it is now found that alcohols, amides, oximes, etc. show a high degree of association in all except the most dilute solutions in a solvent such as carbon tetrachloride, where the infrared technique is particularly satisfactory. The great difficulty is that the polar molecules are nearly insoluble in non-polar solvents. In order to work in polar solvents it is necessary to use very thin films.

The apparent importance of the hydrogen bond in biology is so far-reaching that one may easily be carried away in his enthusiasm over the possible implication of this coupling force. Not only do the large "molecules" found in nature appear to be held together by shared protons, but the gel-like structures formed by these "molecules" in combination with water would seem to depend on the same valence force for their stability. If this is true some of the most fundamental biological problems should yield to obvious methods of attack, methods based on a theory of the valence forces rather than an empirical study of unexplained properties.

Many years ago Dolezalek (2) attempted to account for all deviations from Raoult's law in solutions by assuming association of one or both compounds. He carried this idea to absurd lengths. The recent work of Zellhoefer, Copley, and Marvel (12) on solubilities of organic substances shows, however, that Dolezalek was right in a surprising number of cases. They have been able to show in every case where the solubility is abnormal and there is a possibility of hydrogen bond formation that this fact alone will account for the abnormality. Particularly interesting cases arise when one component is capable of forming hydrogen bonds, both with itself and with the other component.

Polar liquids

The behavior of polar liquids has constituted a no-man's land for the theory of dielectrics, in striking contrast to the achievements of this theory in other directions. Onsager has recently taken into account some effects overlooked by Debye, which apparently give satisfactory results for the strictly nonassociated polar molecules, e.g., nitrobenzene (5). For those molecules which are associated and capable of forming hydrogen bonds no purely electrical theory is likely to be adequate.

The fact that there are two types of association was emphasized many

years ago by Latimer and Rodebush (3). The one type exemplified by the carboxylic acids involves the formation of dimers with zero dipole moment and a resulting non-polar liquid. On the other hand, water, alcohols, some amides, etc. form polymers which are probably chain-like in their arrangement. The polymers form a liquid phase of high dielectric constant with a tendency to form a glass at low temperatures. As yet not very much is known about the mechanism or structure of this polymer formation.

WHAT ATOMS CAN FORM HYDROGEN BONDS?

The picture of the bond given earlier in this paper is that of a hydrogen atom which is somewhat acidic being attracted to a pair of electrons belonging to a somewhat basic atom. If, however, the hydrogen is too acidic and the acceptor atom too basic, salt formation occurs, as with hydrogen chloride and ammonia. What appear to be limiting cases are given by the complexes formed between hydrogen chloride and ether on the one hand and chloroform and ether on the other. The hydrogen of chloroform does appear to us to be very active, but here we are evidently dealing with something analogous to the case of hydrogen iodide; in the presence of an acceptor atom the hydrogen may become very much more polar. But we do not as yet know how to predict this behavior. For example, we have been unable to show any tendency toward hydrogen bond formation on the part of the hydrogen of aniline by the infrared study, yet the N—H bond in aniline must have a larger moment than the C—H bond in chloroform. This brings up a final question about which we know very little, namely, the necessary condition for the hydrogen bonding between two like molecules. We know that the acid amides are strongly associated, as are practically all molecules containing hydroxyl, but that aniline, for example, is much less so, although other evidence indicates some association in various types of amines, including aniline and liquid ammonia itself. There is a very interesting class of complexes of the type formed between picric acid and anthracene. Here the evidence indicates a hydrogen bond, but the shift in the frequency of the hydrogen of the anthracene is so small that it has only been observed upon the high-dispersion echelette-grating spectrometer in this laboratory. One would scarcely think of anthracene as containing an acidic hydrogen, but it is possible that a study of acidic and basic ionization constants under the proper conditions and in the proper solvents might lead to correlations which make possible the prediction of hydrogen bond formation in each instance where it occurs.

REFERENCES

- (1) HILBERT, G. E., WULF, O. R., HENDRICKS, S. B., AND LIDDELL, U.: *J. Am. Chem. Soc.* **58**, 248 (1936).

- (2) HILDEBRAND, J. H.: Solubility of Non-electrolytes, Chap. IV. American Chemical Society Monograph, Reinhold Publishing Corporation, New York (1936).
- (3) LATIMER, W. M., AND RODEBUSH, W. H.: J. Am. Chem. Soc. **42**, 1419 (1920).
- (4) MAASS, O., AND MORRISON, D. M.: J. Am. Chem. Soc. **45**, 1675 (1923).
- (5) ONSAGER, L.: J. Am. Chem. Soc. **58**, 1486 (1936).
- (6) PAULING, L., AND BROCKWAY, L. O.: Proc. Natl. Acad. Sci. U. S. **20**, 336 (1934).
- (7) RODEBUSH, W. H.: Trans. Faraday Soc. **30**, 778 (1934).
- (8) RODEBUSH, W. H., AND MICHALEK, J. C.: J. Am. Chem. Soc. **51**, 748 (1929).
- (9) SLEATOR, W. W., AND PLYLER, E. K.: Phys. Rev. **37**, 1493 (1931).
- (10) VENKATESWARAN, C. S.: Proc. Indian. Acad. Sci. **7**, 13 (1938).
- (11) WRINCH, D. M.: Proc. Roy. Soc. (London) **A160**, 59 (1937).
- (12) ZELLOEFER, G. F., COPLEY, M. J., AND MARVEL, C. S.: J. Am. Chem. Soc. **60**, 1343 (1938).

NON-COULOMBIC INTERACTIONS IN SOLUTIONS OF ELECTROLYTES¹

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INTRODUCTION

The present accepted theory of electrolytic solutions, as developed by Debye and Hückel, Onsager, and Bjerrum, accounts remarkably well for the properties of dilute electrolytic solutions on the basis of Coulombic interaction between the ions. The extension of this theory beyond the range of ordinary conditions has occupied the attention of physicists and physical chemists to such an extent that sight has been lost of many other interactions which, in certain cases, play a significant rôle in determining the properties of solutions of electrolytes. In this connection it is hardly necessary to recall the weaker acids and bases whose strength in aqueous solution is dependent upon the constitution of the substances in question. There are even salts which are weak electrolytes in aqueous solution and to account for whose properties it will doubtless be found necessary to take into consideration interactions other than the purely Coulombic.

It is not the purpose of this paper to enter into a discussion of aqueous solutions of acids, bases, and salts, for there is already an extensive literature relating to this subject. It is in non-aqueous solutions that certain interactions of the non-Coulombic type may be studied with particular ease under conditions that permit of simple interpretation of the observed results. It is proposed to discuss several distinct classes of substances: first, acids and bases; second, weak salts; third, salts involving protonic interaction; and fourth, salts having ions containing dipoles.

ACIDS AND BASES

In an aqueous solution the controlling factor that determines the strength of acids and bases as electrolytes is an active proton, due either to the dissolved substance or to the solvent molecules, which leads to interaction between the molecules of solute and of solvent. Water functions both as

¹ Presented at the Symposium on Intermolecular Action, held at Brown University, Providence, Rhode Island, December 27-29, 1938, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society.

acid and as base, as a result of which solutions of acids and bases in water differ from solutions of the same substances in most non-aqueous media. When a base, such as pyridine, is dissolved in a medium which has no active proton, there is no interaction and the solution shows no electrolytic properties. When, on the other hand, it is dissolved in a medium which has active protons, interaction occurs and the solution exhibits electrolytic properties.

An acid may exhibit electrolytic properties whether the solvent in which it is dissolved has or has not an affinity for a proton of the acid. When the affinity of the solvent molecules for the proton is high, stable positive ions are formed and the solution of the acid exhibits the properties of a normal electrolyte, its strength being primarily determined by the size and configuration of the ions. This, for example, is the case for solutions of acids in liquid ammonia, where the ammonium ion is very stable and there is no essential difference between the properties of ammonium salts and of corresponding salts of other ions such as the ions of the alkali metals.

When an acid is dissolved in a medium which has no affinity for the proton, the properties of the resulting solution are largely determined by quantum forces acting between the proton and the negative constituent of the acid. With a few exceptions such solutions are extremely weak electrolytes, even when the dielectric constant of the solvent medium is high. Thus, hydrogen chloride dissolved in nitrobenzene, of dielectric constant 35, is a very weak electrolyte, while perchloric acid dissolved in the same solvent is a rather strong electrolyte. Obviously the energy necessary to separate the proton from the perchlorate ion, due to quantum forces, is much lower than the corresponding energy in the case of hydrogen chloride. As yet there are too few reliable data relating to the properties of solutions of acids in solvents having no affinity for the proton to enable us to obtain a clear picture of the underlying mechanism of their dissociation into ions.

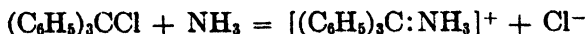
WEAK SALTS

Salts of strongly electropositive ions with negative ions behave like typical electrolytes in all solvents, regardless of whether the negative ion is strongly or weakly negative. The dissociation constant depends upon governing parameters, such as dielectric constant and temperature, and upon the energy necessary to separate the ions from their ion pairs under the action of Coulomb forces. Thus, in liquid ammonia sodium triphenylgermanide, or even sodium triphenylmethide, is a much stronger electrolyte than is sodium chloride, the reason for this being that the triphenylgermanide ion is much larger than the chloride ion and the energy necessary to separate the two ions due to Coulomb forces is correspondingly lower.

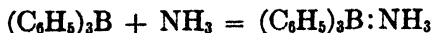
In the case of salts of weakly positive constituents with strongly negative constituents the situation is a different one. These electrolytes are weaker

the less electropositive the positive constituent. The weakly positive ions, in general, have a valence greater than unity, and this change in valence complicates a study of the relationship between the strength of the electrolyte and the electropositeness of the positive constituent. This difficulty may be overcome by satisfying all but one of the valences of the positive constituent by organic groups, leaving only one valence that may have electropolar properties. Thus we have such substances as methylmercury chloride, trimethyltin chloride, triphenylmethyl chloride, and the like. These substances, as a rule, are soluble in water, as well as in other solvents, and form electrolytic solutions, although they are always more or less hydrolyzed in aqueous solutions and sometimes the degree of hydrolysis is too high to permit of their study. All these substances may conveniently be studied in solution in non-aqueous solvents. Trimethyltin chloride is only a moderately strong electrolyte in ethyl alcohol solution, having a dissociation constant of 0.35×10^{-4} . Other substances of this type in alcohol, or other suitable solvents, are distinctly weaker electrolytes than are normal salts, indicating that quantum forces are involved.

When substances of the type of trimethyltin chloride or triphenylmethyl chloride are dissolved in a solvent medium, the appearance of electrolytic properties depends upon interaction between the positive constituent of the compound and the solvent molecules. As stated, trimethyltin chloride is a fairly good electrolyte when dissolved in ethyl alcohol (dielectric constant 26), but it is a very weak electrolyte when dissolved in nitrobenzene (dielectric constant 35). So, also, triphenylmethyl chloride is a good electrolyte in liquid ammonia, of dielectric constant 22, but a very poor electrolyte in nitrobenzene. The interaction which occurs is illustrated by the following equation:



The reaction is closely analogous to the corresponding reaction between triphenylboron and ammonia, which takes place as follows:



The only difference between the two is that in one case the complex formed is positively charged and in the other case it is neutral. A compound such as triphenylmethyl chloride, if dissolved in an inactive solvent of high dielectric constant, may exhibit electrolytic properties if the energy necessary to separate the two constituents is not too high. This energy is dependent upon the quantum forces involved. When this energy is small, as it is in the case of certain groups, electrolytic properties result. Thus, while triphenylmethyl chloride is a very poor electrolyte in nitrobenzene solution, triphenylmethyl perchlorate is a rather good electrolyte. In this

respect the triphenylmethyl compounds, as well as other similar compounds, resemble the corresponding acids which were mentioned above.

SALTS INVOLVING PROTON INTERACTION

Any negative ion tends to interact with an active proton attached to a positive ion. The extent to which such interaction may influence the properties of the resulting solution will depend upon the nature of the solvent molecules themselves. When a partially substituted ammonium salt is dissolved in a solvent medium the molecules of which have no affinity for the proton, interaction takes place between the negative ion and the proton of the positive ion. In other words, there is formed what is commonly known as a hydrogen bond, the energy of rupture of which may be much higher than the energy necessary to overcome the Coulombic forces acting between the ions. When, on the other hand, the same substance is dissolved in a solvent which has a marked affinity for the proton, such as ammonia, the electrolyte behaves normally and in solution will be as strong as any normal electrolyte having ions of the same size.

In table 1 are given dissociation constants for a number of ammonium salts dissolved in nitrobenzene, ethylene chloride, and pyridine, respectively, together with the constants for several quaternary salts in the same solvent.

Considering, first, substituted ammonium picrates in nitrobenzene, it will be noted that the dissociation constants for monobutyl- and dibutylammonium picrates have practically the same value, 1.5×10^{-4} . The dissociation constant of ammonium picrate in the same solvent has not been precisely determined, but it cannot differ from this value by more than a few per cent. On substituting the third hydrogen of the ammonium ion by a butyl group, the dissociation constant is raised to 1.9×10^{-4} , indicating that the energy due to Coulombic interaction is appreciable although small. That the Coulombic forces affect the energy appreciably is shown, moreover, by the fact that the dissociation constant of trimethylammonium picrate is 1.46×10^{-4} , which is about 25 per cent lower than the dissociation constant of tributylammonium picrate. The dissociation constant of tetrabutylammonium picrate is greater than 0.2; the substitution of the last hydrogen of the ammonium group, therefore, raises the constant approximately one thousand times.

The dissociation constant of butylammonium perchlorate is 25.2×10^{-4} , as against 1.50×10^{-4} for the corresponding picrate. Here we see the influence of the markedly weaker affinity of the perchlorate ion for the proton as compared with that of the picrate ion.

In ethylene chloride the influence of the proton closely parallels that found in benzene. Tetramethylammonium picrate has a dissociation constant of 0.326×10^{-4} in ethylene chloride, while pyridonium picrate

has a dissociation constant of approximately 4×10^{-8} . Again, the dissociation constant of a quarternary salt is approximately one thousand times greater than that of the partially substituted ammonium salt. It is interesting to note that pyridonium perchlorate has a dissociation constant of 50×10^{-8} (approx.), which is in accord with the results found for perchlorates and picrates in nitrobenzene.

All the ammonium type of salts when dissolved in pyridine have a nearly normal dissociation constant. Thus, pyridonium nitrate has a dissociation constant of 0.51×10^{-4} , while phenylpyridonium picrate has a dissociation constant of 11.5×10^{-4} . The nitrates are generally somewhat weaker than the picrates because of the smaller size of the nitrate ion, but

TABLE 1
*Dissociation constants of electrolytes in different solvents**

SALT	SOLVENT	K
Ammonium picrate	Nitrobenzene	1.5×10^{-4} (approx.)
Butylammonium picrate	Nitrobenzene	1.50×10^{-4}
Dibutylammonium picrate	Nitrobenzene	1.51×10^{-4}
Tributylammonium picrate	Nitrobenzene	1.90×10^{-4}
Trimethylammonium picrate	Nitrobenzene	1.46×10^{-4}
Tetrabutylammonium picrate	Nitrobenzene	>0.2
Butylammonium perchlorate	Nitrobenzene	25.2×10^{-4}
Pyridonium picrate	Ethylene chloride	4×10^{-8} (approx.)
Pyridonium perchlorate	Ethylene chloride	50×10^{-8} (approx.)
Tetramethylammonium picrate	Ethylene chloride	0.326×10^{-4}
Pyridonium nitrate	Pyridine	0.509×10^{-4}
Piperidonium nitrate	Pyridine	0.184×10^{-4}
Phenylpyridonium picrate	Pyridine	11.5×10^{-4}
Ammonium picrate	Pyridine	2.87×10^{-4}

* The values presented in tables 1 and 2 are due to Messrs. J. B. Ramsey, E. G. Taylor, D. J. Mead, I. M. Tucker, and C. R. Witschonke. Details will be published in due course.

the value obtained for pyridonium nitrate may indicate a slight interaction of the proton with the nitrate ion. Piperidonium nitrate, quite surprisingly, has a dissociation constant of 0.184×10^{-4} , indicating an interaction due to the proton. Apparently a proton interaction is influenced somewhat by the saturation or unsaturation of the groups attached to nitrogen. The dissociation constant of ammonium picrate is 2.87×10^{-4} , indicating that ammonium picrate is a normal type of electrolyte when dissolved in pyridine.

Taking into account the difference in the behavior of ammonium salts in pyridine and in nitrobenzene or ethylene chloride, it seems clear that the low value of the dissociation constants in the latter solvents is due to

interaction between the negative ion and the proton of the positive ion. The absence of such interaction in the case of pyridine solutions is doubtless due to the fact that, because of the relatively high affinity of the pyridine molecule for the proton, the interaction of the proton of the positive ion takes place with a pyridine molecule rather than with a negative ion.

SALTS OF POSITIVE IONS CONTAINING DIPOLES

Heretofore we have had very little information as to the possible influence of substituents other than alkyl or aryl groups in positive ions. All salts are so highly dissociated in water that aqueous solutions do not lend themselves to a study of the relation between constitution and dissociation constant. In solvents of lower dielectric constant, the dissociation constants of salts may be readily determined and the influence of various substituents may be investigated.

Choline, hydroxyethyltrimethylammonium hydroxide, is a base in which one hydrogen of the ethyl group of ethyltrimethylammonium hydroxide has been substituted by a hydroxyl group. It gives rise to a series of salts which are known as choline salts. Other atoms or groups of atoms may be similarly substituted. Thus the halogens (chlorine, bromine, and iodine) may be substituted in place of the hydroxyl group in the case of the normal choline salts. Many similar substitutions may be made.

In table 2 are given dissociation constants for a number of salts of the choline type, dissolved in nitrobenzene, ethylene chloride, and pyridine.

Considering, first, solutions of various choline salts in nitrobenzene, it will be observed that there is a marked decrease in the dissociation constant due to the hydroxyl group. Thus, ethyltrimethylammonium picrate has a dissociation constant of 575×10^{-4} , while hydroxyethyltrimethylammonium picrate has a dissociation constant of 67×10^{-4} . The corresponding methyl derivative is markedly stronger, having a dissociation constant of 199×10^{-4} . Methoxytrimethylammonium picrate and methoxymethyltrimethylammonium picrate have dissociation constants of 269×10^{-4} and 262×10^{-4} , respectively, indicating a slight, and nearly identical, effect due to the introduction of the polar groups $\text{CH}_3\text{O}-$ and CH_3OCH_2- .

In ethylene chloride the relationships are similar to those just described in nitrobenzene. The dissociation constant of ethyltrimethylammonium picrate is 0.46×10^{-4} , while that of choline picrate is 0.066×10^{-4} . In this solvent the hydroxymethyltrimethylammonium picrate, having a constant of 0.088×10^{-4} , is again stronger than the corresponding ethyl derivative. There seems to be a rather close parallelism between the dissociation constants in nitrobenzene and in ethylene chloride.

It is interesting, also, to note the dissociation constants of some of the

halogen-substituted cholines, such as bromoethylcholine picrate, with a dissociation constant of 0.132×10^{-4} , and bromomethylcholine picrate, whose constant is 0.078×10^{-4} . Other cholines have been measured with results similar to those given above.

When dissolved in pyridine the cholines seem to have normal strength. For example, ethyltrimethylammonium picrate has a dissociation constant of 8.2×10^{-4} , while hydroxyethyltrimethylammonium picrate has a dissociation constant of 9.5×10^{-4} . The hydroxymethyl compound, having a dissociation constant of 5.5×10^{-4} , is distinctly weaker than the corresponding ethyl derivative. Both bromoethyltrimethylammonium picrate and bromomethyltrimethylammonium picrate are distinctly weaker than choline picrate.

TABLE 2
Dissociation constants of some choline salts

SALT	$K \times 10^4$		
	Nitrobenzene	Ethylene chloride	Pyridine
Tetrabutylammonium picrate	>0.2*	2.18	12.2
Hydroxyethyltrimethylammonium picrate	67.0	0.0659	9.49
Hydroxymethyltrimethylammonium picrate	199.0	0.0879	5.55
Phenylhydroxydimethylammonium picrate	0.177		12.27
Hydroxytrimethylammonium picrate	0.173		
Methoxytrimethylammonium picrate	269.0		
Methoxymethyltrimethylammonium picrate	262.0	0.254	
Bromoethyltrimethylammonium picrate		0.132	5.85
Bromomethyltrimethylammonium picrate		0.078	4.79
Ethyltrimethylammonium picrate	575.0	0.460	8.21

* Actual value.

At first sight, one would be inclined to ascribe the lower dissociation constant of the choline type of salts to the presence of dipoles in the positive ion. These might well affect the energy of separation of the ion pairs to an appreciable extent. On the other hand, it remains to account for the fact that in the case of pyridine the cholines have normal strength. This would rather seem to indicate that an interaction which occurs in nitrobenzene and in ethylene chloride does not occur in pyridine. In this respect the choline salts resemble the partially substituted ammonium salts in their behavior, although to a much lesser degree.

Very striking are the values found for phenylhydroxydimethylammonium picrate and hydroxytrimethylammonium picrate in nitrobenzene, the constants having values of 0.177×10^{-4} and 0.173×10^{-4} , respectively. The dissociation constants of these salts are about one-tenth that

of the corresponding partially substituted ammonium salts. In pyridine phenylhydroxydimethylammonium picrate has a dissociation constant of 12.27; if anything, it is a rather strong salt in that solvent. This indicates that low values of the dissociation constants of these electrolytes in nitrobenzene are probably due to interaction of the negative ions with the proton of the hydroxyl group attached to nitrogen. When this group is attached to a carbon atom which, in turn, is attached to nitrogen, the dissociation constant is much higher, as in the case of hydroxymethyltrimethylammonium picrate, for which $K = 199 \times 10^{-4}$. It seems, therefore, that the two last named compounds should be classed with the ammonium type of compounds, in that their interaction appears to be due to the presence of an active proton located in the positive ion.

ION CONDUCTANCES IN WATER-METHANOL MIXTURES¹

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INTRODUCTION

It is a part of the program of this laboratory to study thermodynamic and other properties of electrolytes in non-aqueous solvents by the methods (12) that we have already used for aqueous solutions. These methods included E.M.F. measurements of cells with transference, conductances, and measurements of transference numbers by means of moving boundaries. It has been found, however, that the extension of the last-mentioned method to non-aqueous solvents introduces a number of difficulties. For example, most non-aqueous solutions have lower conductances than the corresponding aqueous solutions, with the result that boundary disturbances due to thermal convection are more serious in these solvents than in water. It seemed desirable, therefore, to test the moving-boundary method in water-methanol mixtures where the transition from aqueous to non-aqueous solvents could be made gradually. Using "autogenic" boundaries, a cadmium anode and narrow tubes, we were able to obtain satisfactory cation boundaries with sodium and lithium chlorides in solvents having a methanol mole fraction of 0.8 or less. The boundaries in pure methanol, however, were distorted and did not give reproducible values. This difficulty has not yet been overcome. The data obtained in the aqueous methanol solutions are reported below. The viscosities of water-methanol mixtures were also determined, since the existing viscosity data are insufficient for correlation with the observed ion conductances.

EXPERIMENTAL

The methanol used in this research was a synthetic product which was refluxed and distilled from anhydrous copper sulfate. The specific conductance and density of the distillate were 1.1×10^{-7} mhos and 0.78657 g. per cubic centimeter at 25°C., respectively. Accepting 0.78653 (10) as

¹ Presented at the Symposium on Intermolecular Action, held at Brown University, Providence, Rhode Island, December 27-29, 1938, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society.

the density of pure methanol, our sample contained 0.024 mole per cent of water, which was taken into account in computing the mole fractions of the various mixtures prepared from this material.

The densities of the solvents and solutions were measured to about 0.002 per cent in the pycnometer described in connection with our transference measurements in mixtures of light and heavy water (11). The values for the water-methanol mixtures agreed satisfactorily with those of Gibson (9) throughout the entire range of composition.

The apparatus and methods used in the transference number determinations were similar to those used for aqueous solutions of lanthanum chloride and have been fully described (13, 14).

TABLE 1

Transference and conductance measurements of solutions of sodium and lithium chlorides in water-methanol mixtures at 25°C.

$N_{\text{CH}_3\text{OH}}$	CONCENTRATION	T_+	Λ
Sodium chloride			
0.0000	0.05000	0.3876	111.05
0.1015	0.05006	0.4049	77.08
0.2022	0.04998	0.4182	62.20
0.4020	0.05062	0.4306	53.47
0.6027	0.05002	0.4411	53.12
0.8007	0.05008	0.4475	55.78
Lithium chloride			
0.0000	0.05000	0.3211	100.14
0.1006	0.05130	0.3242	67.85
0.2008	0.05146	0.3292	54.03
0.4027	0.05177	0.3412	46.24
0.6020	0.05019	0.3601	46.52
0.8024	0.05054	0.3804	49.75

The observed cation transference numbers, T_+ , of approximately 0.05 normal solutions of sodium and lithium chlorides are recorded in the third column of table 1. The first column of this table contains the mole fraction of methanol, $N_{\text{CH}_3\text{OH}}$, in the mixture used as solvent for the salts and the second column the exact salt concentration of the solution in equivalents per liter. Owing to a lack of density data no volume correction (13) has been applied to the transference numbers of table 1. At a salt concentration of 0.05 normal, however, this correction does not change the values by more than a few hundredths of a per cent.

The reliability of the transference data of table 1 was indicated by the following facts. There was strict proportionality between the volume

displacement of the boundary and the quantity of electricity passed. The boundaries were not distorted. The transference numbers were found to be independent of the current density used and of the diameter of the tube in which the boundaries were observed.

The equivalent conductances, Λ , of all solutions used in transference experiments were measured on the bridge described by Shedlovsky (16) and are recorded in the last column of table 1. The corrections which would be necessary in order to reduce these values to a concentration of exactly 0.05 normal are small enough not to affect any of the conclusions of this paper. The conductivity cell, with truncated cone electrodes, had a constant of 7.6353 on the basis of 0.012856 for 0.1 demal potassium chloride at 25°C.

The viscosity measurements were made with the aid of a quartz viscometer of the type described by Washburn and Williams (20). The instrument was filled with the aid of a filtering weight buret especially designed for the purpose. A working volume of approximately 50 ml. was used, the exact value being determined from the weight of liquid drawn from the buret. Correction of the time of efflux for water to the actual volume was made with the aid of the experimentally determined relation

$$\text{efflux time for H}_2\text{O} = 363.07 + 0.468 (\text{working volume} - 50)$$

The viscometer constants, which are necessary in making the kinetic energy correction, are as follows: length of capillary, 17.4 cm.; diameter of capillary, 0.0540 cm.; average head, 20.1 cm.; efflux volume, 9.50 ml.

A special design of the viscometer support provided a rapid and convenient method for obtaining a reproducible position of the instrument in the thermostat. The viscometer was permanently mounted in a brass frame provided with three hardened steel pins as shown at a, b, and c in figure 1. These pins were the points of contact between the frame and the rigid supporting arm, A. Pin a rests in a conical hole in the hardened steel block a', b in a v-shaped groove in b', and c presses against a polished steel disc c'. With this arrangement the viscometer automatically comes to rest in the thermostat in a definite position.

The time of efflux was measured with a counter reading directly to 0.01 sec. and driven through a clutch by a synchronous motor. Efflux times for successive fillings exhibited an average deviation from the mean of 0.02 per cent.

The results of the viscosity measurements are recorded in table 2. In this table the mole fractions of the mixtures are given in the first column and their densities in column 2. Owing to the magnitude and uncertainty of the kinetic energy correction we have reported in the third column of the table the values of the ratio, td/t_0d_0 , in which d denotes density and t the

time of efflux, the subscripts referring to water. In applying the correction to this ratio a value of 1.12 for m in the general viscosity equation (3) was used. The relative viscosities, corrected for kinetic energy but not for surface tension, are recorded in the last column of table 2. A short extrapolation gives a value of $\eta/\eta_0 = 0.6050$ for pure methanol. This may be compared with the value 0.6056, also uncorrected for surface ten-

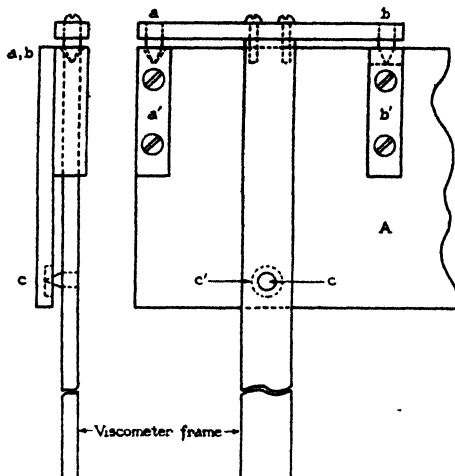


FIG. 1. The viscometer support

TABLE 2

Viscosity measurements of water-methanol mixtures at 25°C.

$N_{\text{CH}_3\text{OH}}$	$d_{4}^{25^\circ}$	$\frac{td}{td_0}$	$\frac{\eta}{\eta_0}$
0.0509	0.98196	1.2520	1.2556
0.1014	0.96946	1.4779	1.4842
0.2015	0.94708	1.7437	1.7529
0.4020	0.90243	1.6567	1.6654
0.6027	0.85997	1.2913	1.2966
0.7954	0.82242	0.9310	0.9325
0.8945	0.80461	0.7630	0.7623
0.9992	0.78666	0.6091	0.6060

sion, obtained by Jones and Fornwalt (10) in a viscometer similar to ours. The discrepancy between the two values probably arises from differences in the computation of the kinetic energy correction.

DISCUSSION OF RESULTS

From the data of table 1 the conductances of the ion constituents, $\lambda = T\Lambda$, have been computed and the results are given in table 3. In

correlating ion conductances with the viscosity of the solvent it is desirable to use the limiting conductances, λ_0 , thereby eliminating the effects of ion-ion interaction. Since the three ions listed in table 3 were found to behave similarly in water-methanol mixtures, we have selected the lithium ion as example in the following discussion. Approximate values of λ_0 for this ion in each of the mixtures have been computed and are given in the last column of the table. These computations were made with the aid of the assumption that $1/\lambda$ varies linearly with \sqrt{C} and has the theoretical slope (17). Sufficient data are available to test the validity of this extrapolation in water and in methanol. The tests indicate that values of λ_0 computed in this manner are not in error by more than about 1 per cent, the error being greatest in the water-rich mixtures.

In figure 2 curve A shows the variation of λ_0 for the lithium ion with the mole fraction of methanol. Curve B indicates the corresponding variation of the viscosity of the solvent. It will be observed that whereas curve

TABLE 3
Ion conductances in water-methanol mixtures at 25°C.

$N_{\text{CH}_3\text{OH}}$	$\lambda_{\text{NaCl}}^{\text{Na}}$	$\lambda_{\text{LiCl}}^{\text{Li}}$	$\lambda_{\text{NaCl}}^{\text{Cl}}$	$\lambda_{\text{LiCl}}^{\text{Cl}}$	$\lambda_{0\text{Li}}$
0.0	43.04	32.15	68.01	67.99	39.3
0.1	31.21	22.00	45.87	45.85	27.2
0.2	26.01	17.79	36.19	36.24	22.4
0.4	23.02	15.78	30.45	30.46	20.9
0.6	23.43	16.75	29.69	29.77	23.7
0.8	24.96	18.92	30.82	30.82	28.9

A is concave to the mole fraction axis curve B is convex to this axis. If Walden's rule,

$$\lambda_0 \cdot \eta = \text{constant}$$

were valid a plot of the product of the ordinates of these two curves would be a horizontal line. The actual values of this product are plotted in curve C and it will be seen that, after a slight maximum in water-rich mixtures, the curve is linear with a sharp descent. Walden's rule, based as it is on Stokes' law, tacitly assumes that the size of the ion-solvent complex is independent of the medium. The trend of curve C indicates that the lithium-ion complex increases in size with increasing mole fraction of methanol.

Walden's rule appears to be valid for large ions (18), such as the tetra-alkylammonium ions, whose fields are, presumably, too weak to orient solvent dipoles. However, Born (5) and Schmick (15) have shown that the fields about small ions are sufficiently intense to orient dipoles of the solvent about them and hold at least a portion of these solvent molecules.

It is not surprising, therefore, that the Walden rule is not applicable to these ion-solvent complexes, since the customary methods of testing the rule, i.e., variation of the viscosity by changes of temperature, pressure, solvent, etc., are almost certainly accompanied by changes in this complex.

Additional evidence for an increase in the size of the lithium ion-solvent complex with increasing mole fraction of methanol may be obtained from a consideration of the apparent molal volume of lithium chloride in solution. Thus the salt has an apparent volume of 17.0 ml. in water (8) and -3.8 ml. in methanol (19), whereas the molal volume in the crystal is 20.5 ml. The contraction occurring on solution in water has been explained (2) as due to orientation of water dipoles about the ions, the solvent molecules

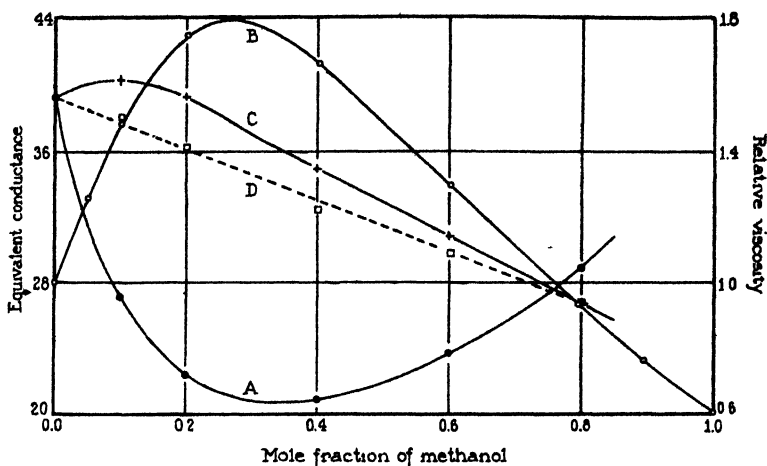


FIG. 2. Ion conductance-viscosity relations in water-methanol mixtures. Curve A, limiting conductances, λ_0 , of the lithium ion. Curve B, relative viscosities, $\frac{\eta}{\eta_0}$, of the solvent mixtures. Curve C, a plot of the $\lambda_0 \cdot \frac{\eta}{\eta_0}$ product. Curve D, a plot of the $\lambda_0 \left(\frac{\eta}{\eta_0} \right)^{0.86}$ product.

of the ion-water complex being more closely packed, presumably, than in normal water. The still greater contraction observed in methanol suggests that the ion-methanol complex is larger than the ion-water complex.

In the $\lambda \frac{\eta}{\eta_0} - N_{\text{CH}_3\text{OH}}$ curves for each of the three ions studied, a slight maximum occurs in the water-rich mixtures, being more pronounced for the sodium ion than for the lithium and chloride ions. In terms of the hypothesis discussed in the preceding paragraphs this would indicate a slight decrease in the size of the ion-solvent complex compared with its value in water. It is in this region of solvent composition that the com-

ponents exhibit the largest deviations from Raoult's law, indicating considerable interaction. It does not seem improbable that this dipole-dipole interaction occurs at the expense of the ion-dipole interaction, thereby reducing slightly the size of the ion-water complex. Empirically, the maximum in curve C of figure 2 disappears if the viscosity is raised to a fractional power. Thus $\lambda_0 \left(\frac{\eta}{\eta_0} \right)^{0.86}$ is very nearly linear with the mole fraction as shown by curve D. This is also true for the data on the chloride and sodium ions. Though frequently used, no theoretical justification of these fractional exponents has been advanced.

Additivity of ion conductances in water-methanol mixtures

As indicated in columns 4 and 5 of table 3, the agreement between the chloride-ion conductances of the two alkali chlorides furnishes striking evidence of the *equal* ionization of these two salts in a given water-methanol mixture. These salts are completely dissociated in water, and it seems reasonable to assume that they are also completely dissociated in the water-methanol mixtures. This assumption is obviously the simplest explanation of the observed additivity of ion conductances. It is also in agreement with modern theories of ionic solutions. For example, Fuoss and Kraus (7), in their extension of the Bjerrum concept (4) of ion association, point out that in a solvent of a given dielectric constant ions above a certain critical size cannot form pairs. This size, a , "the Bjerrum distance," is given by the relation

$$a = \frac{e^2}{2DkT}$$

in which the symbols have their usual significance. For water at 25°C. $a = 3.5 \text{ \AA.}$, while for a water-methanol mixture of $N_{\text{CH}_3\text{OH}} = 0.8$ and a dielectric constant of 37.7 (1), $a = 7.4 \text{ \AA.}$ Thus, in terms of this theory the sums of the radii of the solvated anion and cation must be at least 3.5 Å. in water and 7.4 Å. in the mixture for which $N_{\text{CH}_3\text{OH}} = 0.8$ if no ion pairs are to be formed.

Brown and MacInnes (6) obtained 4.45 Å. as the distance of closest approach for the ions of sodium chloride in water from an application of the Debye-Hückel equation to their activity measurements. Similar measurements are not available for water-methanol mixtures, but if we can assume that the $\lambda_0\eta$ product is a measure of the size of the ion-solvent complex a tentative value of a for sodium chloride in the mixture for which $N_{\text{CH}_3\text{OH}} = 0.8$ may be computed from the relation

$$a(N_{\text{CH}_3\text{OH}} = 0.8) = \frac{\Lambda_0\eta(N_{\text{CH}_3\text{OH}} = 0.0)}{\Lambda_0\eta(N_{\text{CH}_3\text{OH}} = 0.8)} 4.45$$

The value thus computed is 7.77 Å. This is somewhat larger than the critical size of 7.4 Å., which is necessary if no ion pairs are to be formed. Consequently our conclusion that sodium and lithium chlorides are completely dissociated in water-methanol mixtures is in apparent agreement with the theories of Bjerrum and of Fuoss and Kraus.

SUMMARY

Transference and conductance measurements of 0.05 normal solutions of sodium and lithium chlorides in water-methanol mixtures have been made, together with determinations of viscosity. The product of the equivalent ion conductance and the viscosity deviates greatly from Walden's rule and indicates increasing size of the ion-solvent complex with increasing methanol concentration.

In a given solvent the chloride-ion conductances of the two salts are very nearly equal. This is in accord with the assumption of the complete dissociation of sodium and lithium chlorides in these solvents.

REFERENCES

- (1) ÅKERLÖF, G.: J. Am. Chem. Soc. **54**, 4125 (1932).
- (2) BERNAL, J. D., AND FOWLER, R. H.: J. Chem. Phys. **1**, 515 (1933).
- (3) BINGHAM, E. C.: Fluidity and Plasticity. McGraw-Hill Book Co., Inc., New York (1922).
- (4) BJERRUM, N.: Kgl. Danske Videnskab. Selskab. **7**, No. 9, 2 (1926).
- (5) BORN, M.: Z. Physik **1**, 221 (1920).
- (6) BROWN, A. S., AND MACINNES, D. A.: J. Am. Chem. Soc. **57**, 1356 (1935).
- (7) FUOSS, R. M., AND KRAUS, C. A.: J. Am. Chem. Soc. **55**, 1019 (1933).
- (8) GEFFCKEN, W.: Z. physik. Chem. **A155**, 1 (1931).
- (9) GIBSON, R. E.: J. Am. Chem. Soc. **57**, 1551 (1935).
- (10) JONES, G., AND FORNWALT, H. J.: J. Am. Chem. Soc. **60**, 1683 (1938).
- (11) LONGSWORTH, L. G., AND MACINNES, D. A.: J. Am. Chem. Soc. **59**, 1666 (1937).
- (12) MACINNES, D. A.: Science **86**, 23 (1937).
- (13) MACINNES, D. A., AND LONGSWORTH, L. G.: Chem. Rev. **11**, 171 (1932).
- (14) MACINNES, D. A., AND LONGSWORTH, L. G.: J. Am. Chem. Soc., forthcoming publication.
- (15) SCHMICK, H.: Z. Physik **24**, 56 (1924).
- (16) SHEDLOVSKY, T.: J. Am. Chem. Soc. **52**, 1793 (1930).
- (17) SHEDLOVSKY, T.: J. Franklin Inst. **225**, 739 (1938).
- (18) ULICH, H.: Fortschr. Chem. Physik physik. Chem. **18**, 567 (1926).
- (19) VOSBURGH, W. C., CONNELL, L. C., AND BUTLER, J. A. V.: J. Chem. Soc. **1933**, 933.
- (20) WASHBURN, E. W., AND WILLIAMS, G. Y.: J. Am. Chem. Soc. **35**, 737 (1913).

THERMODYNAMICS OF STRONG ELECTROLYTES IN PROTIUM OXIDE-DEUTERIUM OXIDE MIXTURES. I¹

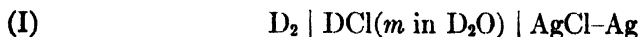
HYDROGEN CHLORIDE

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In their pioneer investigation on the dissociation constant of heavy water, Abel, Bratu, and Redlich (1) measured the cell



Although correctly treated in principle, the limited amounts of heavy water available at that time rendered measurements difficult. Furthermore, at the conclusion of their investigation these authors recognized that their results at intermediate deuterium concentrations were uncertain, owing to the fact that the gas bubbled over the electrode differed in deuterium content from that in equilibrium with the solvent (8). The interpretation of the small E.M.F. differences when the atom fraction of deuterium in the solvent, designated as F_D or n , is varied requires a higher order of precision than they were able to obtain.

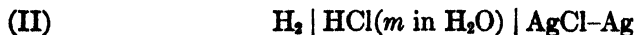
We have measured cell I at 25°C. over a wide range of deuterium content with a microcell employing the principle of the Clark rocking electrode (4). This type of cell possesses an advantage for work with heavy water in that it is possible to start with a small volume of pure hydrogen and to establish the exchange equilibrium between the gas phase and the bulk of the solvent of a given deuterium content in a reasonable time by means of the platinized electrode. Under these conditions the same E.M.F.'s are obtained when either pure deuterium or pure hydrogen is the initial gas phase. Furthermore the gas is conserved, the pressure on the closed system can be carefully regulated, and the complete removal of oxygen is effected.

Aside from the inherent interest in the thermodynamics of deuterium chloride in deuterium oxide, a precise value for E^0 of cell I is necessary for the determination of dissociation constants of acids in deuterium oxide,

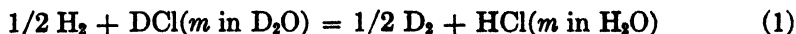
¹ Presented at the Symposium on Intermolecular Action, held at Brown University, Providence, Rhode Island, December 27-29, 1938, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society.

as well as the dissociation constant of deuterium oxide itself, from cells without transference, using the deuterium gas electrode.

By subtracting cell I from the corresponding cell II, employing protium oxide as the solvent



the free energy change of the following process may be determined.



Abel, Bratu, and Redlich (1) obtained 3.4 millivolts for the E.M.F. of process 1 when extrapolated to pure deuterium oxide. Their results also indicated that there might be a maximum in the E.M.F. of process 1, as written above as a function of the deuterium content of the solvent. A single measurement of Drucker (5), when $F_D = 0.89$, yielded the value 5.4 millivolts, suggesting that this maximum might be greater than was previously suspected (8).

Confusion has appeared in the recent literature in an attempt to reconcile Schwarzenbach, Epprecht, and Erlenmeyer's (14) value of -2.2 millivolts for a cell with transference with Abel, Bratu, and Redlich's value of 3.4 millivolts (13). This investigation was undertaken to refine and clarify the knowledge of the behavior of hydrogen chloride in protium oxide-deuterium oxide mixtures.

EXPERIMENTAL

Dry hydrogen chloride gas was passed into heavy water until the concentration reached 9 per cent. This stock solution was analyzed gravimetrically at the beginning and end of the research; it remained constant to 6 parts in 10,000, corresponding to an uncertainty in the E.M.F. of ± 0.02 millivolt. Heavy water was purified by molecular distillation *in vacuo* from alkali and then from potassium dichromate, organic matter being removed when necessary by heating with alkaline permanganate. Density determinations were made in a combined pycnometer and conductance cell. The specific conductance of the water was less than 2×10^{-6} mhos. The water was transferred directly from the pycnometer to a small flask and weighed. Deuterium chloride stock solution was added from a micro weight buret. The solution was then boiled *in vacuo* to remove oxygen, 1 to 2 per cent of the water being evaporated in the process. Deuterium or hydrogen at atmospheric pressure was admitted to the flask, and the loss of weight determined. Pyrex glass apparatus with interchangeable ground joints was used throughout this investigation, and all parts were carefully cleaned and steamed before use.

The double cell illustrated in figure 1 was attached to an electrically driven mechanism which rocked it about the glass joint A as an axis.

Each cell had two silver chloride and two hydrogen electrodes. Hydrogen was admitted through the stopcock B and the connection A, the fixed inner member being connected to a supply of gas at constant pressure slightly higher than atmospheric. After the electrodes were in place the cell was filled by connecting the filling flask at C and an empty receiving flask at D, and evacuating the system repeatedly with a Hyvac pump. After all water was evaporated from the electrodes the cell was flushed twice with hydrogen or deuterium and the stopcocks closed under vacuum, so that the solution could be admitted to the silver chloride compartments.

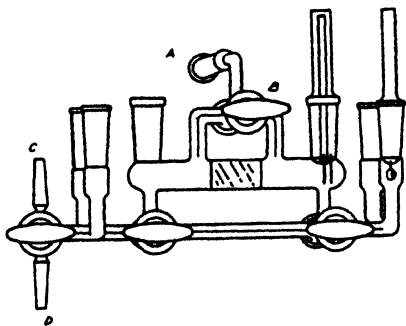


FIG. 1

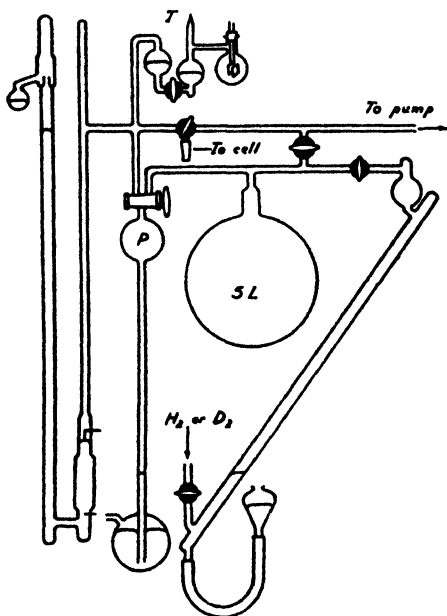


FIG. 2

FIG. 1. The double cell

FIG. 2. Manostat and gas storage system

After 30 min. this solution was drawn off into a receiving flask, and more solution was run into the cell. The horizontal compartments were half filled, and hydrogen was admitted. The flasks were replaced by caps and the cell transferred to a thermostat. Sixteen milliliters of solution was sufficient to wash the electrodes once and to fill the cell. The limited quantities of heavy water available for washing constitute one of the serious restrictions upon the precision of the results. Scrupulous cleanliness and care in avoiding contamination of the electrodes with films of stopcock grease are essential.

Two hydrogen electrodes, consisting of 22 B. & S. gauge platinum wires

1 cm. long, were sealed through a soft-glass 12/30 standard taper inner member, as detailed. Silver chloride electrodes were deposited on platinum wires sealed through 10/30 standard taper soft-glass joints. The electrode holders were the only parts of the apparatus made of soft glass; their area was small compared to the total glass surface. Two types of silver chloride electrodes were used. The electrolytic type described by Brown (3) yielded highly reproducible results at the temperature of preparation, 25°C., but gave unreliable temperature coefficients, probably owing to strains in the layers of silver and silver chloride. Electrodes of the annealed thermal type described by Rule and La Mer (11) are not quite as reproducible at 25°C., but yield more consistent temperature coefficients and are simpler to prepare. The electrolytic type electrodes were not washed in the cell, but were soaked overnight in conductivity water before use. The influence of all these variations in electrode technique was within the experimental error, as shown by figure 3 and the accompanying legend.

Constant pressure of hydrogen or deuterium was maintained to ± 0.2 mm. of mercury by a manostat, which is shown, together with the gas storage system, in figure 2. Contacts sealed in the manometer operated a relay connected to an electrolytic cell, and gas pressure from this cell was transmitted through a mercury seal to the hydrogen system. Excess pressure was released through the capillary tip T. The length of the manometric mercury column can be adjusted over a wide range by distilling mercury from the storage bulb on the vacuum side, or by forcing it out of the tip. The stopcock B was opened for about 5 sec. between readings to equilibrate the pressure, but was kept closed at other times to prevent distillation of the solvent and to avoid equilibration of all gas in the manometer system. All readings are corrected to 760 mm. of mercury at 0°C.

The hydrogen and deuterium were prepared by electrolysis. Each gas was passed over hot copper, the water was frozen out, and the gas was bubbled through an inclined mercury column into an evacuated 5-liter storage flask. In this manner the gas can be generated at atmospheric pressure and collected at pressures ranging from zero to atmospheric. The inclined tube should be at least 15 mm. in diameter, and the splash bulb is advisable. After starting, the process proceeds smoothly and requires little attention. The gas was transferred to the manostat system by means of a Toepler pump, P. The storage system was checked from time to time for leaks.

The electrical measuring equipment and thermostatic facilities have been described previously (12). The six independent voltages obtained from the double cell were averaged as the final reading. At 25°C. readings were started about 4 hr. after preparation, continued for 6 hr., and checked

after a 24- to 30-hr. period. Readings over this period agreed to 0.02 millivolt in most cases. To minimize hysteresis, temperature changes were made slowly at a rate of 5°C . over a 2-hr. period. Constant readings were always obtained within 15 min. after reaching constant temperature, except at 5°C . and 10°C . Three readings at half-hour intervals were taken at constant temperature.

The rate of attainment of exchange equilibrium between the gas and solvent cannot be estimated from the change in E.M.F., since an unknown time is required to saturate the solution with gas. Starting with pure hydrogen and a solvent containing 64 per cent D, equilibrium was reached in 30 min. after the cell was filled and rocking started. The same equilibrium values are obtained starting with either pure hydrogen or deuterium, as shown by figure 3 and legend.

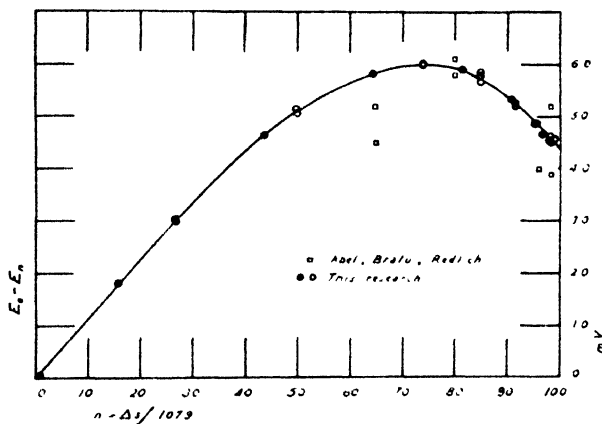


FIG. 3. E.M.F. of process 1 plotted as a function of the deuterium content of the solvent. ●, initially pure H_2 gas and thermal silver chloride electrodes; ○, initially pure D_2 gas and electrolytic silver chloride electrodes

The concentration of hydrogen chloride was reduced to a uniform molal basis by calculating moles of chloride ion per 55.51 gram-atoms of oxygen in the solvent. The vapor pressure of pure deuterium oxide was taken from the data of Miles and Menzies (9). Linear variation of the vapor pressure of the solvent with deuterium content was assumed.² Corrections were made for the light water introduced from the stock solution and for the water evaporated during evacuation. Weights were reduced to weights *in vacuo*, and corrections were applied for the buoyancy of

² The changes in vapor pressure with deuterium content will be linear only if the vapor pressure of HDO is the mean of protium oxide and deuterium oxide. Results of Stedman (Can. J. Research 13B, 114 (1935)) indicate a sagged curve, but the deviation is certainly within 1 mm. of mercury or ± 0.02 millivolt.

hydrogen or deuterium replacing air in the flask. E.M.F. values in light water at corresponding molalities were interpolated from the data of Harned and Ehlers (7).

The subscript n in E_n refers to the fraction of deuterium in the solvent defined as $F_D = n = \Delta s/0.1079$; $0 < n < 1$. Thus E_0 is an E.M.F. in pure water; $E_{0.4}$ an E.M.F. when $F_D = 0.4$. The superscript zero indicates a molal potential, i.e., the E.M.F. has been corrected to a hypothetical molal activity of the solute equal to unity.

It is impractical to obtain E_n^0 by measuring an extensive series of cells at varying acid concentrations and extrapolating to infinite dilution while the deuterium concentration is kept constant. The difference $E_0 - E_n$ was measured at a concentration of about 0.03 to 0.04 molal. E_n^0 was found by assuming that the change in interionic activity coefficient with concentration is the same in light and in heavy water, with an allowance for the minor difference in dielectric constants of protium oxide and deuterium oxide. Defining H_2 and D_2 at 760 mm. as the standard gaseous state, and letting γ represent the mean interionic activity coefficient, referred to infinite dilution in protium oxide and deuterium oxide as unity, then

$$E_0 = E_0^0 - 2RT/F \ln \gamma_{HCl(H_2O)}$$

$$E_1 = E_0^0 - 2RT/F \ln \gamma_{DCl(D_2O)}$$

Through the equation

$$\log \gamma = -A(\mu)^{1/2}$$

we obtain

$$E_0^0 - E_1^0 = E_0 - E_1 + \frac{2(2.3)RT}{nF} (A_{D_2O} - A_{H_2O})(\mu)^{1/2}$$

Values of A in the Debye-Huckel limiting law for protium oxide and deuterium oxide have been calculated from the recent dielectric constant data of Wyman and Ingalls (15), and are presented in table 1.

Experimental data at 25°C. are presented in table 2. The $E_0^0 - E_n^0$ values are given only for large values of n . Calculations of $E_0^0 - E_n^0$ for lower values of n were not made, because of a possible uncertainty in the dielectric constants of solvents containing large amounts of the unsymmetrical HDO. The E.M.F. of process 1 is plotted in figure 3 as a function of the deuterium content of the solvent; a pronounced maximum occurs at $n = 0.75$. The extrapolated value in 100 per cent deuterium oxide for $E_0^0 - E_1^0$ is 0.00447 volt; the E^0 value for cell I is therefore 0.21792, compared to the value of 0.22239 volt given by Harned and Ehlers (7) for cell II at 25°C.

TABLE 1
Values of A for protium oxide and deuterium oxide

TEMPERATURE	A_{H_2O}	A_{D_2O}	$\frac{(4.6) RT}{F} (A_{D_2O} - A_{H_2O})$
°C.			
5	0.489	0.492	0.00024
10	0.493	0.496	0.00026
15	0.498	0.500	0.00027
20	0.502	0.504	0.00031
25	0.506	0.509	0.00033
30	0.511	0.514	0.00035
35	0.516	0.519	0.00038
40	0.521	0.524	0.00041
45	0.527	0.530	0.00044

TABLE 2
Electromotive force of the cell
 $H_2 | (HCl\ DCl)_m \text{ in } H_2O\text{-}D_2O | AgCl\text{-}Ag$
at 25°C. in protium-deuterium oxide mixtures of deuterium
fraction n and molality m

n	m	E_o $F_D = 0$	E_n $F_D = n$	$E_o - E_n$	$E_o^0 - E_n^0$
0.989	0.02883	0.41247	0.40792	+0.00455	0.00461
0.986	0.03282	0.40620	0.40164	0.00456	0.00462
0.984	0.04607	0.38984	0.38532	0.00452	0.00459
0.984	0.01626	0.44031	0.43574	0.00457	0.00461
0.982	0.02991	0.41071	0.40610	0.00461	0.00467
0.966	0.03287	0.40614	0.40148	0.00466	0.00472
0.956	0.05927	0.37769	0.37286	0.00483	0.00491
0.955	0.03190	0.40758	0.40271	0.00487	0.00493
0.954	0.15233	0.33204	0.32722	0.00482*	0.00495
0.915	0.03030	0.41007	0.40480	0.00527	
0.915	0.03378	0.40480	0.39958	0.00522	
0.909	0.03419	0.40423	0.39890	0.00533	
0.848	0.03322	0.40562	0.39977	0.00578	
0.848	0.03826	0.39880	0.39312	0.00568	
0.848	0.04028	0.39632	0.39047	0.00585	
0.848	0.04428	0.39176	0.38609	0.00567	
0.813	0.03341	0.40534	0.39946	0.00588	
0.813	0.03182	0.40770	0.40180	0.00590	
0.739	0.02817	0.41360	0.40758	0.00602	
0.739	0.03158	0.40806	0.40206	0.00600	
0.644	0.02901	0.41218	0.40636	0.00582	
0.523	0.03417	0.40626	0.39920	0.00506	
0.522	0.03239	0.40684	0.40169	0.00515	
0.436	0.03148	0.40823	0.40360	0.00463	
0.268	0.03595	0.40181	0.39882	0.00299	
0.266	0.02899	0.41220	0.40918	0.00302	
0.158	0.03115	0.40873	0.40691	0.00182	
0.008	0.02555	0.41831	0.41826	0.00005	

* In plotting results were corrected to 0.03 m.

TABLE 3
Temperature coefficient data

$\Delta s/0.1079$	m	TEMPERATURE	E_0 $F_D = 0$	E_0 $F_D = 1$	$E_0 - E_n$	$E_0^0 - E_1^0$
		°C.				
0.982	0.02991	25	0.41071	0.40610	0.00461	0.00467
		30	0.41066	0.40589	0.00477	0.00483
		35	0.41044	0.40550	0.00494	0.00501
		40	0.41004	0.40498	0.00506	0.00513
		45	0.40957	0.40424	0.00533	0.00541
0.986	0.03282	5	0.40521	0.40090	0.00431	0.00435
		10	0.40579	0.40111	0.00468	0.00473
		15	0.40599	0.40176	0.00423	0.00428
		20	0.40612	0.40181	0.00431	0.00436
		25	0.40620	0.40164	0.00456	0.00462
0.956	0.05926	5	0.37848	0.37410	0.00438	0.00444
		10	0.37858	0.37403	0.00452	0.00458
		15	0.37837	0.37390	0.00447	0.00454
		20	0.37807	0.37348	0.00459	0.00467
		25	0.37769	0.37286	0.00483	0.00491
		30	0.37709	0.37212	0.00497	0.00506
		35	0.37639	0.37121	0.00518	0.00527
		40	0.37545	0.37015	0.00530	0.00540
0.955	0.03190	45	0.37445	0.36892	0.00553	0.00565
		5	0.40651	0.40204	0.00449	0.00453
		10	0.40709	0.40251	0.00458	0.00462
		15	0.40732	0.40270	0.00462	0.00467
		20	0.40753	0.40286	0.00463	0.00469
		25	0.40758	0.40271	0.00487	0.00493
		30	0.40753	0.40243	0.00506	0.00512
		35	0.40718	0.40199	0.00525	0.00532
		40	0.40678	0.40130	0.00548	0.00555

TABLE 4
Thermodynamic quantities at 25°C. for the process
 $1/2 \text{H}_2 + \text{DCl}(\text{D}_2\text{O}) = 1/2 \text{D}_2 + \text{HCl}(\text{H}_2\text{O})$

$\Delta s/0.1079$	$E_0^0 - E_1^0$	$-\Delta F$	ΔS	ΔH
	volts	Calories	Cal. deg.	Calories
0.955	0.00493	113.7	1.00	184
0.956	0.00491	113.2	0.87	146
0.982	0.00467	107.7	0.81	133
0.986	0.00462	106.5	0.82	137
1.0 (extrap.)	0.00447	103.1	0.75	120

Experimental results of cell I at the various temperatures are given in table 3. At the lower temperatures the data in both light and heavy water are less reliable, and the differences correspondingly less certain. The thermodynamic quantities for process 1 listed in table 4 have been evaluated at 25°C. by numerical differentiation of the data from 15°C. to 45°C. The dependence of ΔS and ΔH on the deuterium content of the solvent indicates that a maximum for these quantities will exist similar to ΔF , as shown in figure 3.

The data for $10^5 E_n/T$ for $m = 0.05926$ when $n = 0$ and when $n = 0.956$ are plotted against $1/T$ in figure 4. The slope of the resulting curve is a

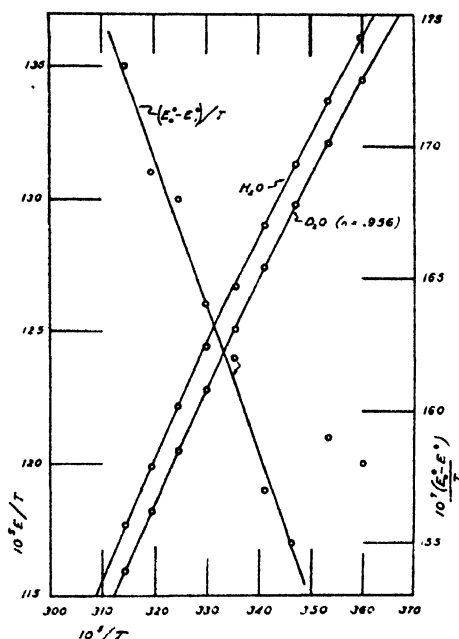


FIG. 4. The temperature dependence of E.M.F. of cells I and II and process 1 plotted as E/T against $1/T$.

direct measure of ΔH for the corresponding cell process. Since both the light and the heavy water data fall on smooth parallel curves, ΔC_p is not zero for the process involving the silver chloride electrode in either solvent, as would be expected.

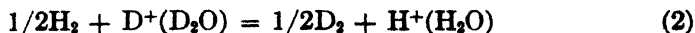
On the other hand, when the sensitive difference function

$$10^7(E_0^0 - E_1^0)/T$$

is plotted against $1/T$, a straight line results except for the two less certain points at the lowest temperatures. ΔC_p for the exchange process 1 is

accordingly very small if not actually zero, i.e., ΔH is practically independent of temperature.

For theoretical purposes the equilibrium constant of the reaction



is frequently desired. The free energy change of process 2 differs from that of process 1 by the process



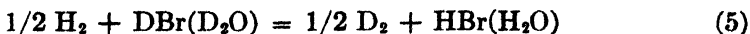
representing the difference in free energy of solvation of chloride ions in light and heavy water. This process, however, is inaccessible to experimental determination, a point which will be elaborated in another paper. Gross and Wischin (6) have mistaken process 1 for process 2 in their theoretical treatment. Orr and Butler (10) utilize process 1 for the calculation of the constant L of their semi-empirical equation for equilibria in isotopic mixtures, but are obliged to ignore the effect of chloride ions.

Abel and Redlich (2) emphasize that the exchange process 1 is not the "normal potential" of the deuterium gas electrode. *In order to ascribe a value for the normal potential of deuterium it is necessary that the half-cell process proceed in the same solvent, H_2O , for which the normal potential of H_2 is taken arbitrarily as zero.* The specification that the process must be conducted throughout in protium oxide as the solvent is impossible to meet experimentally on account of the rapid exchange of gases with solvent on platinum black as the catalyst. The closest approach would be given by the process

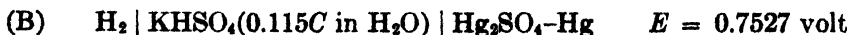
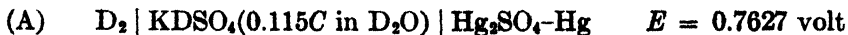


when the concentration of H_2DO^+ is made negligibly small. On the basis of process 4 Abel and Redlich compute a normal potential for deuterium which is approximately 44 millivolts less noble than hydrogen. We also subscribe to their view that little is to be gained by attempting to define a normal potential of the deuterium electrode against the hydrogen electrode.

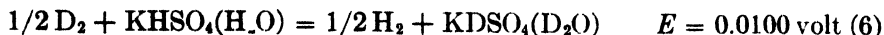
If silver bromide electrodes and hydrobromic acid had been used in cell I the following process could be obtained



The free energy of this process would differ from that of process 2 by the difference in the free energy of solvation of bromide and chloride ions in the two solvents. A somewhat more complicated process has been measured by Drucker (5).



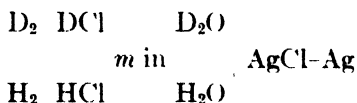
The net process for cell A minus cell B is



Taking the second dissociation constant of sulfuric acid as 2×10^{-2} , the hydrogen-ion concentration in a solution of potassium hydrogen sulfate 0.115*C* in H_2O is 0.059*C*. From the empirical curve of Rule and La Mer (12) the dissociation constant of DSO_4^- is estimated as 2.5 times less than that of HSO_4^- or 8×10^{-3} . Applying the mass law, the deuterium-ion concentration in a solution of potassium deuterium sulfate 0.115*C* in deuterium oxide is 0.035*C*. After considering the contribution to the E.M.F. difference of cells A and B due to the concentration of hydrogen and deuterium ions, respectively, the E.M.F. of the combination still has a different sign from the E.M.F. of process 1 as a result of the specific differences in the free energy of solvation of chloride, sulfate, and potassium ions.

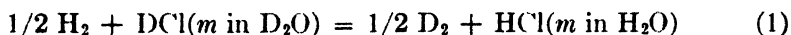
SUMMARY

1. The cell without transference



has been studied at 25°C. over a wide range of deuterium content. The E^0 value at 100 per cent deuterium oxide is 0.21792 ± 0.00005 volt, or 4.47 millivolts less than for hydrogen chloride in protium oxide.

2. The free energy change of the process



is a complicated function of the deuterium content of the solvent, passing through a maximum at a deuterium fraction 0.75, corresponding to an E.M.F. 6.0 millivolts lower than E^0 in protium oxide.

3. Thermodynamic quantities for process 1 at high deuterium concentrations have been evaluated from temperature coefficient data.

4. With the rocking electrode described, equilibrium between the gas phase and solvent is achieved rapidly, starting with either pure deuterium or hydrogen.

REFERENCES

- (1) ABEL, BRATU, AND REDLICH: *Z. physik. Chem.* **A173**, 353 (1935).
- (2) ABEL AND REDLICH: *Z. Elektrochem.* **44**, 204-5 (1938); cf. reference 1.
- (3) BROWN: *J. Am. Chem. Soc.* **56**, 646 (1934).
- (4) CLARK: *Determination of Hydrogen Ions*, 3rd edition, p. 295. The Williams & Wilkins Co., Baltimore (1928).
- (5) DRUCKER: *Trans. Faraday Soc.* **33**, 660 (1937).

monochromator was directly coupled with a brass box with a light-tight lid. Within the box four absorption cells were mounted on a rotatable disc. The glass absorption cells were made in the form of cylinders 2 cm. in length. One end was an optically plane glass disc fused to the cylinder; the other end of the cell was open, with the edge of the cylinder ground flat. A polished disc of optical glass was placed against this end and was held in position by a metal ring and rubber gasket. The cell, with glass-stoppered side arm, was inserted in a metal tube which could be set into a flange forming an integral part of the disc in the box. By turning a knob outside the box the cells could be brought into the line of light, one at a time.

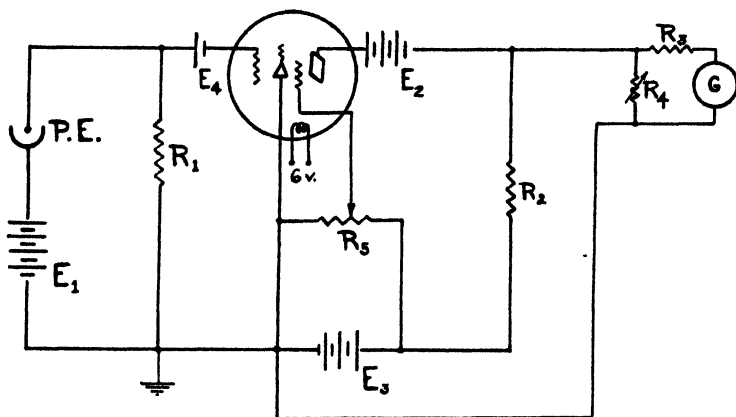


FIG. 1. Diagram of the circuit. G, Leeds and Northrup type R galvanometer, sensitivity = 0.003μ amperes per millimeter, critical damping resistance = 2100 ohms, period = 2.7 sec., resistance = 580 ohms; R_1 , 100-megohm resistor; R_2 , 0.1-megohm resistor; R_3 , 1700-ohm resistor; R_4 , decade box, 0 to 350 ohms; R_5 , 0.2-megohm potentiometer; E_1 , 225 volts; E_2 , 22.5 volts; E_3 , 45 volts; E_4 , 1.5 volts; P.E., photoelectric cell; tube, RCA 1603.

Two photoelectric cells were used,--a potassium hydride cell sensitive in the blue and a cesium cell sensitive in the red portion of the spectrum. The photoelectric cell was connected in the grid circuit of the amplifier as shown in the diagram² (figure 1). It was found that with a grid resistance of 100 megohms adequate sensitivity was obtained with a stable zero. After calibration of the absorption cells, it was found that Beer's law curves could be obtained with a reproducibility of 0.2 per cent.

² The authors take this opportunity to acknowledge the helpful advice of J. P. Hervey of the Eldridge Reeves Johnson Foundation for Medical Physics, University of Pennsylvania, and S. E. Hill, The Rockefeller Institute for Medical Research, New York City, on the design of the circuit.

Preparation of materials

The alcohols were purified by the method of Bjerrum and Lund (2). The dioxane was purified by fractionating in an all-glass column, refluxing over sodium, and distilling.

The sulfonphthalein indicators and the chlorobenzoic acids were special preparations used in other studies (5, 14). The benzoic acid was from the National Bureau of Standards. The monochloroacetic acid was recrystallized from benzene, and the glycolic acid from pure acetone. The dichloroacetic acid was fractionally distilled. The acetic acid, free from homologs, was refluxed with pure acetic anhydride and fractionally distilled. The dinitrophenols, the other acids, and the lithium salts were desiccated Kahlbaum products. All acids were carefully titrated, and melting points were determined to establish their purity.

Preparation of the buffer solutions

Since the majority of the experimental measurements were made in non-aqueous solutions, it was necessary to devise a system for the preparation of buffer solutions which would be economical of solvent. A rack holding four pipets was built, each pipet being connected at the upper end to a vacuum line. The stopcocks were placed at the top of the pipets to keep the solvent away from the lubricant. The 10-ml. pipets were graduated in units of 0.05 ml., the 1-ml. pipet in 0.01 ml. units, and the 0.2-ml. pipet was calibrated in units of 0.001 ml. By using suitable combinations of pipets it was possible to make up the buffer solutions to a volume of 11 ml. In the cases where the lithium salts were available, buffer solutions of convenient acid-base ratios were prepared from the acid and the lithium salt. Otherwise a quantity of base (in the form of sodium hydroxide, lithium methylate, or lithium ethylate) was added to neutralize partially the free acids. The stock buffer was diluted in successive steps by taking measured portions of the solution, diluting to 10 ml., and adding 1 ml. of the indicator solution. For the case where the solvated proton was to be measured, dilute solutions of hydrochloric acid were prepared by passing a stream of dried hydrogen chloride into the pure solvent, titrating a portion with standard alkali, and then adding the indicator. The indicator solutions were made up by dissolving a quantity of the indicator (usually in the form of the acid) in the purified solvent. After addition to the buffer the concentration was approximately 1×10^{-5} moles per liter.

The dioxane-water mixtures required a slightly different method, since the final solution had to contain a known percentage by weight of dioxane in order to give solutions of known dielectric constant, as determined by Åkerlöf and Short (1).

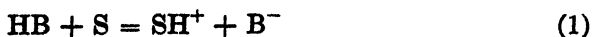
Determination of the absorption curve

In order that the proper wave length could be selected for the measurements, an absorption curve was determined for each indicator in each solvent. This was done in the following manner: Solutions of the completely acid and basic forms of the indicator were prepared and placed in absorption cells. With indicators showing two transition points, care was exercised to avoid interference from a third color by making up the indicator in a suitable buffer solution. A third cell was filled with solvent. Galvanometer deflections were read at different wave lengths, and, by taking the galvanometer reading for the pure solvent as 100 per cent transmission, the absorption was calculated from the readings for the indicator solution. The percentage adsorption was plotted against the wave length for the colored forms, and the wave length corresponding to the peak of the appropriate absorption curve was utilized for subsequent determinations.

Experimental procedure

For each determination four solutions, of different concentrations, of the completely basic (or acidic) form of the indicator were placed in the cells. The decade resistance box was adjusted so that for the proper wave length the most dilute solution gave a deflection of 45 cm. on the galvanometer scale. Galvanometer deflections were then obtained for all four cells, and a Beer's law curve was constructed by plotting the logarithms of the galvanometer readings against the concentrations. The concentrations of indicator were selected so that the reading for the unknown fell between the readings for the standard solutions. Readings were then taken for all four cells, a Beer's law curve was constructed, and the percentage of the acid (or basic) form of the indicator was read off from the graph. All experiments were carried out at $25^{\circ}\text{C.} \pm 2^{\circ}$.

A summary of a typical experiment is given in table 1. Columns 1 and 2 give the stoichiometric concentration of benzoic acid and lithium benzoate in the buffer mixture. To obtain the correct values of the acid-base ratio it is necessary to take into account the reaction with the solvent



The ratio of basic to acid form of the indicator is then calculated from the colorimetric determination and the equilibrium constant for the reaction written at the top of the table

$$K_{\text{AIB}} = \frac{C_{\text{B}_1}}{C_{\text{A}_1}} \cdot \frac{C_{\text{A}}}{C_{\text{B}}} \quad (2)$$

is recorded in column 4.

Now K_{AIB} varies with ionic strength, and the thermodynamic equilibrium constant is obtained by extrapolation, as illustrated in figure 2.

The method for obtaining the values of the other equilibrium constants will be illustrated later. Tables 2, 3, and 4 give the data for the equilibria between the yellow form of bromocresol green and *p*-chlorobenzoate in the solvents methyl alcohol, ethyl alcohol, and dioxane-water mixtures.

It will be noted that the classical dissociation constant of the buffer acid is now so small that it is no longer necessary to correct for the concentra-

TABLE 1
Determination of the equilibrium constant

A_1^-	+	B^-	=	A^0	+	B_1^-
Bromocresol green (yellow)		Benzoate		Benzoic acid		Bromocresol green (blue)

Stoichiometric concentration of indicator = 4×10^{-5} ; $T = 24.5^\circ\text{C}$.; solvent = water

C_A	C_B	$\sqrt{\mu}$	K_{AiB}
<i>moles per liter</i>	<i>moles per liter</i>		
0.009091	0.02727	0.165	0.243
0.004545	0.01364	0.117	0.221
0.002273	0.006818	0.0827	0.208
0.001515	0.004545	0.0676	0.201
0.000909	0.002727	0.0524	0.196

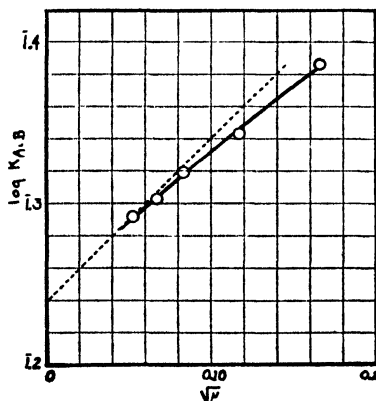


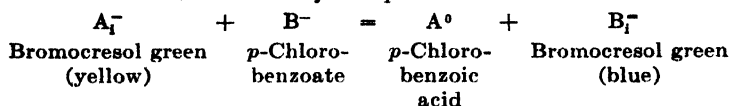
FIG. 2. Bromocresol green-benzoic acid-water

tion of the solvated proton. It should also be noted that the indicator concentration is always small relative to the concentration of the buffer acid. In other words, the addition of the indicator does not appreciably disturb the equilibrium of the buffer.

The relation between the equilibrium constants in the solution and that in the pure solvent is given by

$$[K_{AiB}]_0 = K_{AiB} \frac{f_0 f_2}{f_1 f_i} \quad (3)$$

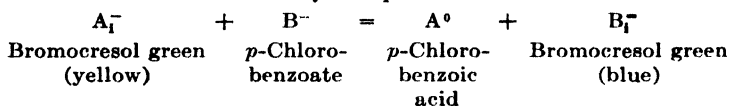
TABLE 2
Determination of the equilibrium constant



Stoichiometric concentration of indicator = 6×10^{-6} ; $T = 23.5^\circ\text{C}$.; solvent = methyl alcohol

C_A	C_B	$\sqrt{\mu}$	K_{A_1B}
<i>moles per liter</i>	<i>moles per liter</i>		
0.02600	0.02600	0.1612	0.557
0.01560	0.01560	0.1249	0.490
0.00780	0.00780	0.08832	0.412
0.00390	0.00390	0.06245	0.356
0.00208	0.00208	0.04560	0.312
0.00104	0.00104	0.03225	0.274

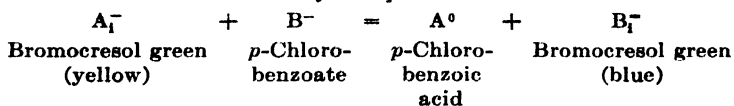
TABLE 3
Determination of the equilibrium constant



Stoichiometric concentration of indicator = 6×10^{-6} ; $T = 27.0^\circ\text{C}$.; solvent = ethyl alcohol

C_A	C_B	$\sqrt{\mu}$	K_{A_1B}
<i>moles per liter</i>	<i>moles per liter</i>		
0.02500	0.02500	0.1581	0.533
0.01250	0.01250	0.1118	0.456
0.00750	0.00750	0.0866	0.402
0.00500	0.00500	0.0707	0.363
0.00250	0.00250	0.0500	0.300
0.00125	0.00125	0.0353	0.259

TABLE 4
Determination of the equilibrium constant



Stoichiometric concentration of indicator = 8×10^{-6} ; $T = 23.5^\circ\text{C}$.; solvent dioxane-water ($D = 25.0$)

C_A	C_B	$\sqrt{\mu}$	K_{A_1B}
<i>moles per liter</i>	<i>moles per liter</i>		
0.03200	0.03200	0.1789	0.279
0.01920	0.01920	0.1386	0.250
0.01280	0.01280	0.1131	0.230
0.00640	0.00640	0.0800	0.198
0.00320	0.00320	0.0566	0.172
0.00192	0.00192	0.0438	0.152
0.00128	0.00128	0.0357	0.1325

where f_i 's represent the activity coefficients. Since, according to the Debye theory,

$$\log f_i = - \frac{1.81 \times 10^6}{D_0 T^{3/2}} Z_i^2 \sqrt{\mu} \quad (4)$$

we have in the limit

$$\log K_{A_1B} = \log [K_{A_1B}]_0 + S\sqrt{\mu} \quad (5)$$

where S is 1.01 for water, 4.22 for methyl alcohol, and 5.64 for ethyl alcohol and dioxane-water mixtures of the same dielectric constant. It is also

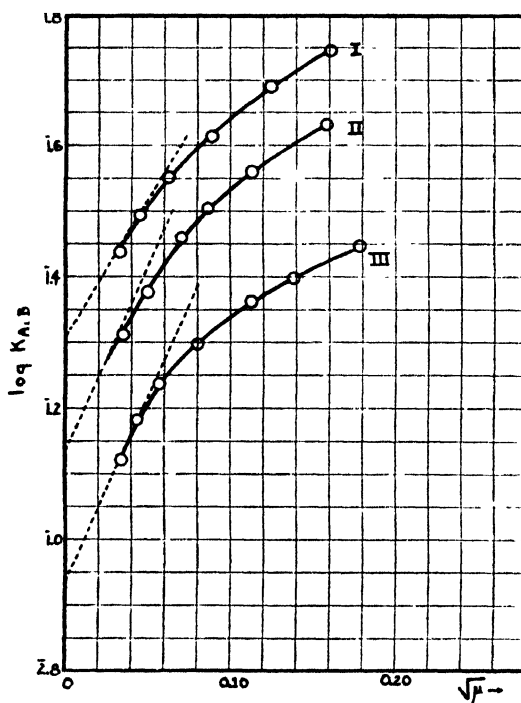


FIG. 3. Extrapolations to infinite dilution. Curve I, bromocresol green-*p*-chlorobenzoic acid-methyl alcohol; curve II, bromocresol green-*p*-chlorobenzoic acid-ethyl alcohol (down 0.1); curve III, bromocresol green-*p*-chlorobenzoic acid-dioxane-water ($D = 25$).

convenient to use a graph of $\log K_{A_1B}$ versus $\frac{\sqrt{\mu}}{1 + \sqrt{\mu}}$ (10), but this involves an assumption of a change in the "average distance of closest approach" for the different solvents. Figures 2 and 3 illustrate the extrapolation for the four solvents. Other charge types involve different slopes, and in the convenient case where the indicator acid and the buffer acid are of the same charge type the Debye terms cancel and we have a

simple extrapolation linear with the concentration. Extrapolations of this type are illustrated in figure 4.

The results for aqueous solution are summarized in table 5. Column 2 lists the equilibrium constants (equation 2) at zero ion concentration for the various acid-base pairs given in column 1. Column 3 gives the logarithm of the equilibrium constant for the reaction



where A_x represents the acid in question and A_0 the standard acid. It is computed from the ratio of the equilibrium constants given in column 2,

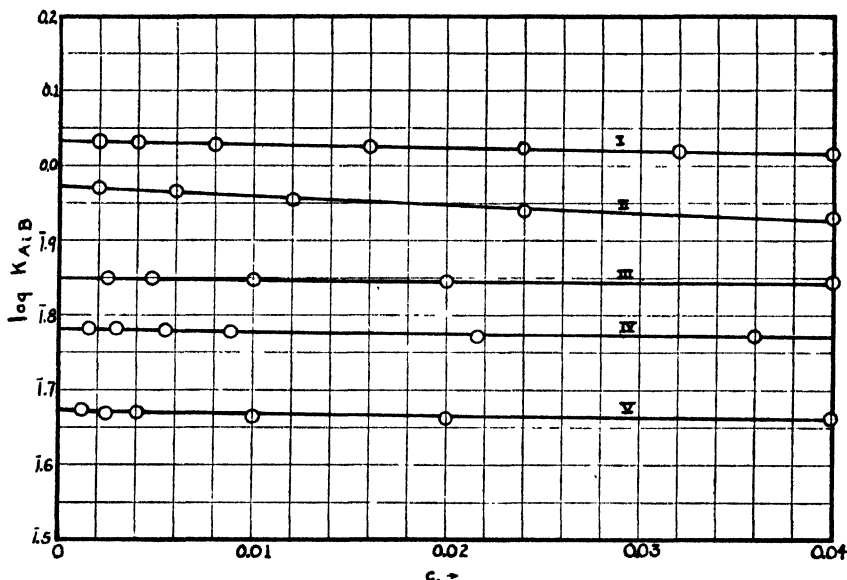


FIG. 4. Extrapolations to infinite dilutions. Curve I, 2,4-dinitrophenol-salicylic acid-methyl alcohol; curve II, 2,4-dinitrophenol-monochloroacetic acid-methyl alcohol; curve III, 2,6-dinitrophenol-monochloroacetic acid-dioxane-water ($D = 25$); curve IV, 2,4-dinitrophenol-salicylic acid-dioxane-water ($D = 25$); curve V, 2,6-dinitrophenol-monochloroacetic acid-water (up 0.6).

benzoic acid being chosen as the standard acid. The values for the chlorobenzoic acids are computed from conductivity data (15). Since the value for the thermodynamic dissociation constant of benzoic acid in water given by Saxton and Meier (15), 6.295×10^{-5} , and that given by Brockman and Kilpatrick (3), 6.312×10^{-5} , are in agreement, pK for benzoic acid is taken as 4.201 to have the chlorobenzoic acids on the same basis. Column 4 gives the negative logarithm of the equilibrium constant

$$K = C_{H_3O^+} \cdot \frac{C_B}{C_A} \quad (7)$$

in water. This scale was established by relating the red-yellow range of the indicator *m*-cresol purple to hydrochloric acid. The extrapolation with a slope of unity gave the value for the dissociation constant (equation 7) of *m*-cresol purple. From the equilibrium constant for *m*-cresol purple and cyanoacetate ion the dissociation constant of cyanoacetic acid was computed, and by a stepwise procedure all the acids in table 5 were determined, with the exception of the halogen-substituted benzoic acids. Com-

TABLE 5
Acid strengths in water

ACIDS	K_{AiB}	$\log K_r$	pK (= $-\log K$)	pK (LITERATURE)
<i>m</i> -Cresol purple (hydrochloric)			1.674	1.5 ⁽¹⁾
Cyanoacetic (<i>m</i> -cresol purple)	8.09	1.630	2.582	2.43 ⁽²⁾
Monochloroacetic (2,6-dinitrophenol)	0.119	1.338	2.874	2.854 ⁽³⁾
<i>o</i> -Chlorobenzoic*		1.279		2.922 ⁽⁹⁾
Salicylic (2,6-dinitrophenol)	0.151	1.234	2.978	2.97 ⁽²⁾
2,6-Dinitrophenol (cyanoacetic)	0.0607	0.413	3.799	3.811 ⁽⁴⁾
<i>m</i> -Chlorobenzoic*		0.379		3.822 ⁽⁹⁾
Glycolic (2,6-dinitrophenol)	1.22	0.327	3.885	3.829 ⁽⁶⁾
<i>p</i> -Chlorobenzoic*		0.219		3.982 ⁽⁹⁾
2,4-Dinitrophenol (glycolic)	0.732	0.191	4.021	4.025 ⁽⁴⁾
Benzoic (bromophenol blue)	0.951	0.000	4.212	4.200 ⁽⁶⁾
Benzoic*		0.000		4.201 ⁽⁶⁾
Bromophenol blue (glycolic)	0.448	-0.022	4.234	4.23 ⁽⁸⁾
Acetic (bromocresol green)	0.627	-0.556	4.768	4.758 ⁽¹⁰⁾
Bromocresol green (benzoic)	0.174	-0.759	4.971	4.94 ⁽⁷⁾

(1) Cohen: Pub. Health Repts. **42**, 3051 (1927) ($\mu = 0.1$).

(2) Landolt-Bornstein Tabellen (Ostwald).

(3) Saxton and Langer: J. Am. Chem. Soc. **55**, 3638 (1933).

(4) von Halban and Kortum: Z. physik. Chem. **A170**, 351 (1934).

(5) J. Böeseken and H. Kalshover: Rec. trav. chim. **37**, 130 (1918).

(6) Brockman and Kilpatrick: J. Am. Chem. Soc. **56**, 1483 (1934).

(7) Kilpatrick: Chem. Rev. **16**, 57 (1935).

(8) Kilpatrick: J. Am. Chem. Soc. **56**, 2048 (1934).

(9) Saxton and Meier: J. Am. Chem. Soc. **56**, 1918 (1934).

(10) MacInnes and Shedlovsky: J. Am. Chem. Soc. **54**, 1429 (1932).

* Saxton and Meier.

parison of columns 4 and 5 shows the agreement between the results obtained by the present method and the values given in the literature. The agreement establishes the reliability of the experimental method.

Table 6 summarizes the results in methyl alcohol. In this solvent the acidity scale was not experimentally related to the solvated proton, owing to the fact that a suitable indicator was not found to relate the acids to the solvated proton. The scale was established indirectly by taking the value for the dissociation constant of benzoic acid as 3.79×10^{-10} (6).

Table 7 summarizes the results in ethyl alcohol. In this case it was possible to establish an acidity scale by referring to the solvated proton,

TABLE 6
Acid strengths in methyl alcohol

ACIDS	K_{AiB}	$\log K_r$	pK ($= -\log K$)	pK (LITERATURE)
Benzoic*			9.422	9.422*
Cyanoacetic (2,4-dinitrophenol)	0.437	1.918	7.504	
2,6-Dinitrophenol (cyanoacetic)	0.692	1.758	7.664	
Monochloroacetic (2,4-dinitrophenol)	0.943	1.584	7.838	
2,4-Dinitrophenol (salicylic)	1.08	1.559	7.863	
Salicylic (bromophenol blue)	0.0922	1.526	7.896	7.880*
<i>o</i> -Chlorobenzoic (bromophenol blue)	0.250	1.092	8.330	
Glycolic (bromophenol blue)	0.686	0.654	8.768	
<i>m</i> -Chlorobenzoic (bromophenol blue)	0.851	0.560	8.862	
Bromophenol blue (benzoic)	3.09	0.490	8.932	
<i>p</i> -Chlorobenzoic (bromocresol green)	0.204	0.300	9.122	
Acetic (bromocresol green)	0.891	-0.340	9.762	
Bromocresol green (benzoic)	0.407	-0.390	9.812	

* Goldschmidt: Z. physik. Chem. **112**, 429 (1924).

TABLE 7
Acid strengths in ethyl alcohol

ACIDS	K_{AiB}	$\log K_r$	pK ($= -\log K$)	pK (LITERATURE)
Benzoic*		0.000	10.13	10.13*
Thymol blue (hydrochloric)			4.77	
Thymol blue (dichloroacetic)	87.6		4.95	
Dichloroacetic (2,4-dinitrophenol)	0.0482	3.238	6.89	
2,4-Dinitrophenol (monochloroacetic)	2.00	1.921	8.21	
Salicylic (bromophenol blue)	0.0672	1.683	8.45	
Monochloroacetic (bromophenol blue)	0.0776	1.620	8.51	
Glycolic (bromophenol blue)	0.447	0.860	9.27	
Bromophenol blue (benzoic)	3.24	0.51	9.62	
<i>p</i> -Chlorobenzoic (bromocresol green)	0.172	0.439	9.69	
Bromocresol green (benzoic)	0.473	-0.325	10.46	
Acetic (bromophenol blue)	0.656	-0.307	10.44	

* Larsson: Dissertation, Lund, 1924.

but the extrapolation of the equilibrium constants for thymol blue (red-yellow) with the solvated proton and with dichloroacetic acid seemed abnormal, and the agreement between the value for benzoic acid (pK_A

(C_2H_5OH) = 9.94) and those of Larsson (12) ($pK_A(C_2H_5OH)$ = 10.13 and 10.40) is not good. In view of this uncertainty in the use of thymol blue, the values given in table 7 (column 4) are related to the solvated proton by Larsson's value of 7.4×10^{-11} for $K_A(C_2H_5OH)$. It should be mentioned that Kolthoff (11) pointed out that thymol blue in aqueous solutions of hydrochloric acid acts as a hybrid ion.

In the use of thymol blue in dioxane-water mixtures no difficulty was encountered, and the acidity scale was established by the stepwise procedure (table 8).

It should again be pointed out that the experiments recorded in this paper were carried out at $25^\circ C. \pm 2^\circ$. The dielectric constants of the

TABLE 8
Acid strengths in dioxane-water
Dielectric constant = 25

ACIDS	K_{AIB}	$\log K_r$	pK (= - $\log K$)
Thymol blue (hydrochloric)			2 726
Dichloroacetic (thymol blue)	18.7	3 009	3 998
Cyanoacetic (2,6-dinitrophenol)	0.272	2.115	4 892
Monochloroacetic (2,6-dinitrophenol)	0.709	1 699	5 308
Salicylic (2,6-dinitrophenol)	0.762	1.668	5 339
2,6-Dinitrophenol (dichloroacetic)	0.0348	1 550	5 457
2,4-Dinitrophenol (salicylic)	0.607	1.451	5.556
<i>o</i> -Chlorobenzoic (bromophenol blue)	0.186	1 044	5 963
Glycolic (bromophenol blue)	0.238	0 937	6.070
<i>m</i> -Chlorobenzoic (bromocresol green)	0.0603	0 542	6 465
<i>p</i> -Chlorobenzoic (bromocresol green)	0.0860	0.388	6.619
Bromophenol blue (monochloroacetic)	0 0412	0 314	6.693
Benzoic (bromophenol blue)	2.060	0.000	7.007
Bromocresol green (benzoic)	0.210	-0.678	7 685
Acetic (bromocresol green)	0.373	-0.250	7.257

solvents vary with temperature, but a consideration of the magnitude of this change indicates that the influence of the temperature upon the dielectric constants may be neglected. The effect of temperature on the dissociation constants of the carboxylic acids may also be neglected over the range of temperature of these experiments.

Columns 3 of tables 5, 6, 7, and 8 give the logarithms of the equilibrium constants for each acid with benzoate ion in the pure solvent in question. These values are independent of the basicity of the solvent, and the relation to the dielectric constant can now be considered. If the dielectric constant of the medium is the important factor affecting K_r , the values in ethyl alcohol and in water-dioxane mixtures should agree. A comparison for carboxylic acids for the two solvents shows quite good agreement.

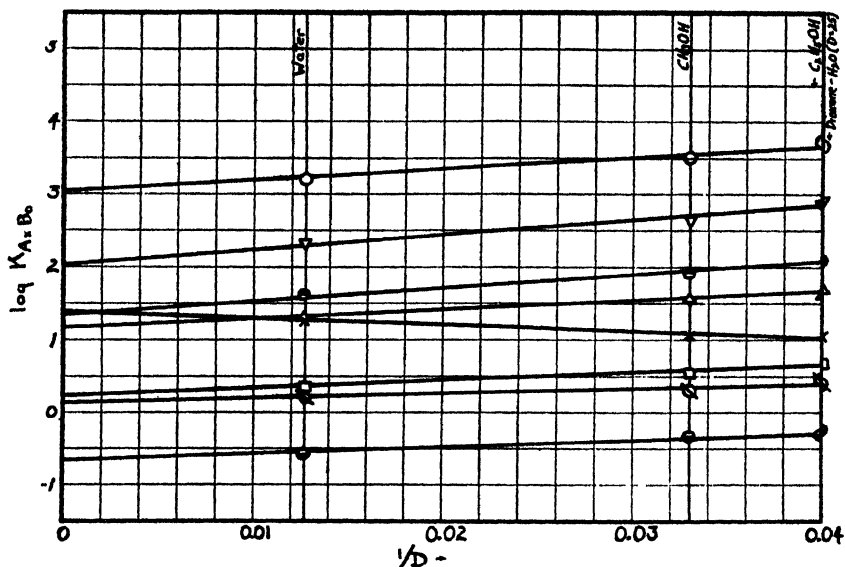


FIG. 5. Plot of $\log K_{A,B_0}$ against $(1/D)$. $D = 80$ to $D = 25$. \ominus , cyanoacetic acid; Δ , monochloroacetic acid; \bigcirc , salicylic acid (up 2.0); \times , *o*-chlorobenzoic acid; ∇ , glycolic acid (up 2.0); \square , *m*-chlorobenzoic acid; \boxtimes , *p*-chlorobenzoic acid; \ominus , acetic acid.

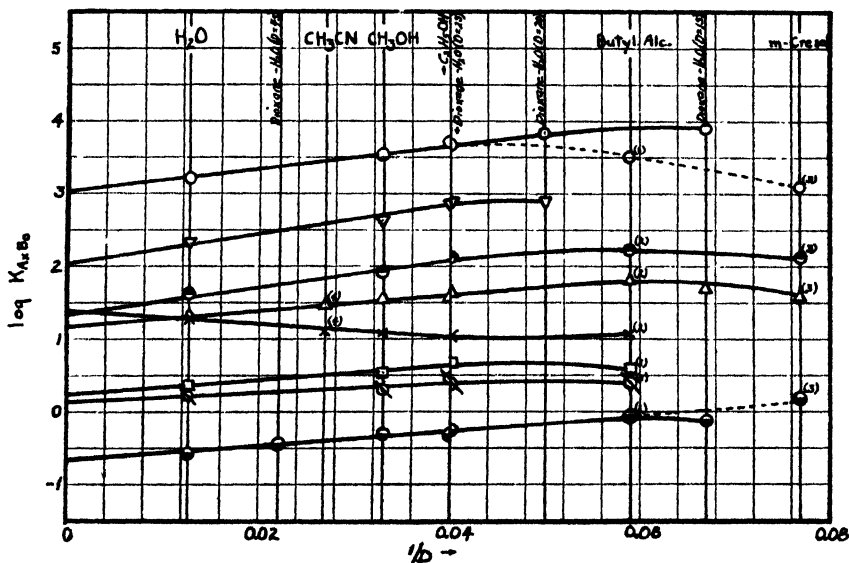


FIG. 6. Plot of $\log K_{A,B_0}$ against $(1/D)$. $D = 80$ to $D = 13$. \ominus , cyanoacetic acid; Δ , monochloroacetic acid; \bigcirc , salicylic acid (up 2.0); ∇ , glycolic acid (up 2.0); \square , *m*-chlorobenzoic acid; \boxtimes , *p*-chlorobenzoic acid; \times , *o*-chlorobenzoic acid; \ominus , acetic acid. ⁽¹⁾ Wooten and Hammett: J. Am. Chem. Soc. **57**, 2289 (1935); ⁽²⁾ Mason and Kilpatrick: J. Am. Chem. Soc. **59**, 572 (1937); ⁽³⁾ Brönsted, Delbanco, and Tovberg-Jensen: Z. physik. Chem. **A169**, 361 (1934); ⁽⁴⁾ Kilpatrick: Unpublished work.

This is illustrated in figure 5. Figure 5 indicates that a plot of $\log K_r$ versus $1/D$ is linear over the range of dielectric constant 80 to 25. Figure 6 shows, however, that this is not the case for media of lower dielectric constant. That lack of linearity is not due to any difference in experimental method is confirmed by the experimental results in dioxane-water mixtures of dielectric constants 15, 20, and 45 given in table 9. Since $\log K_{A_xB_0}$ ($\log K_r$) has been shown to be a function of $1/D$, the results may be expressed by the following empirical equation

$$\log K_{A_xB_0} = \log K_{a_xb_0} + L \left(\frac{1}{D} \right) \quad (8)$$

where $K_{a_xb_0}$ is the intrinsic acid strength and L the slope of the line in figure 5.

TABLE 9
Acid strengths in dioxane-water mixtures

ACIDS	K_{AiB}	$\log K_r$
Dielectric constant = 15		
Benzoic (bromophenol blue)	2.24	0.000
Salicylic (bromophenol blue)	0.0276	1.909
Monochloroacetic (bromophenol blue) ...	0.0458	1.690
<i>m</i> -Chlorobenzoic (bromophenol blue)	0.631	0.550
Acetic (bromophenol blue)	2.95	-0.120
Dielectric constant = 20		
Benzoic (bromophenol blue)	1.59	0.000
Salicylic (bromophenol blue) ...	0.0224	1.851
Dielectric constant = 45		
Benzoic (bromophenol blue)	1.98	0.00
Acetic (bromophenol blue)	5.53	-0.445

The values of $\log K_{a_xb_0}$ and L are given in table 10, and equation 8 holds to within 0.05 log unit of K_r . Equations relating the protolysis constant to the ideal protolysis constant at infinite dielectric have been given by Brönsted (4) and by Hammett (8, 9).³ For any acid, A_x , having the same charge as the standard acid, A_0 , the Brönsted equation becomes

$$\ln K_{A_xB_0} = \ln K_{a_xb_0} + \frac{\epsilon^2(2Z_A - 1)}{2kT} \left[\frac{r_{A_0} - r_{A_x}}{r_{A_0}r_{A_x}} \right] \frac{1}{D} \quad (9)$$

³ Two papers entitled "The Electrostatic Influence of Substituents on the Dissociation Constants of Organic Acids" by Kirkwood and Westheimer (J. Chem. Phys. 6, 507, 513 (1938)) appeared too late for consideration in this paper.

where r_{A_x} and r_{A_0} are the effective radii of the acids, D the dielectric constant, and Z the valence. Reasonable values of r_{A_x} and r_{A_0} give concordant values of $K_{A_xB_0}$ for the carboxylic acids (10). The equation of Hammett

$$\ln K = \ln K_0 - \frac{A'}{kT} \frac{1}{d^2} \left(\frac{B'_1}{D} + B'_2 \right) \quad (10)$$

is similar to equation 9. Here d is the distance from the carboxyl group to the substituent group, K_0 is the equilibrium constant for the standard, and A' depends upon the substituent and its position in the molecule,

TABLE 10
Values of $\log K_{A_xB_0}$ and L

ACIDS	LOG $K_{A_xB_0}$	SLOPE L	$\Delta F_D = \infty$	ΔF SOLVENT = H ₂ O	V_{el}	ΔS SOLVENT = H ₂ O
<i>o</i> -Chlorobenzoic	1.40	-9.0	-1910	-1750	+150	-1.3
Cyanoacetic	1.35	19	-1840	-2220	-330	+2.6
Monochloroacetic	1.18	12	-1610	-1830	-210	+1.7
Salicylic	1.05	15	-1430	-1690	-260	+2.1
<i>m</i> -Chlorobenzoic	0.25	10	-340	-520	-170	+1.5
<i>p</i> -Chlorobenzoic	0.15	6.3	-200	-300	-110	+0.90
Glycolic	0.05	19	-70	-445	-330	+2.7
Acetic	-0.65	9.3	+890	+770	-160	+1.3

while B'_1 and B'_2 depend only on the reaction. Hammett puts the above equation in the form

$$\log K = \log K_0 + \sigma \rho \quad (11)$$

where $\sigma = A/2.303R$ is the substituent constant and

$$\rho = \frac{1}{d^2 T} \left(\frac{B_1}{D} + B_2 \right)$$

is the reaction constant. The values of $\log K_{A_xB_0}$ calculated by equation 11 are in good agreement with the observed values. The equation can be applied at different dielectric constants by using one result to calculate the reaction constant ρ , and from this value and Hammett's value for σ to calculate the $K_{A_xB_0}$ value of another acid. For example, for *m*-chlorobenzoic acid at $D = \infty$,

$$\rho = \frac{\log K_{r_\infty}}{\sigma} = \frac{0.25}{0.373} = 0.67$$

and the calculated value for $\log K_{r_\infty}$ for *p*-chlorobenzoic acid is 0.15, which is identical with the observed value. In methyl alcohol the observed value is 0.30, as against 0.34 by a similar calculation. For a medium of dielec-

tric constant of 25 the calculated value is 0.41, while the observed value in ethyl alcohol is 0.44 and in dioxane-water is 0.39. More data on the substituted benzoic acids are needed in non-aqueous solution.

The free energy of the reaction is given by

$$-\Delta F = 2.30RT \log K_{A_xB_0} = W \quad (12)$$

where W is the work of transferring a proton from one acid to the other. The values of ΔF at $D = \infty$ and in the solvent, water, are given in columns 4 and 5 of table 10. Gurney (7) has accounted for the energy by two effects, the potential energy due to electrostatic (V_{e1}) and to non-electrostatic (V_{non}) forces. The non-electrostatic energy yields the Morse type of curve showing a minimum at a definite distance. This part of the energy is assumed to be independent of temperature and may be evaluated from $K_{A_xB_0}$ at $D = \infty$, where the electrostatic forces do not operate. The electrostatic energy may be evaluated from the experimentally determined slopes of figure 5 by the equation

$$L = \frac{\log K_{A_xB_0} - \log K_{A_xB_0}}{1/D} = \frac{WD}{2.30RT} = \frac{V_{e1}D}{2.30RT} \quad (13)$$

The values of the electrostatic energy are given in column 6 of table 10.

$$V_{e1} = \frac{-2.303LRT}{D} = \frac{AT}{D} \quad (14)$$

where $A \neq f(T)$.

$$\Delta S = \frac{d\Delta F}{dT} = \frac{A}{D} - \frac{AT}{D^2} \frac{dD}{dT} = \frac{V_{e1}}{T} - V_{e1} \frac{d \ln D}{dT} \quad (15)$$

Since $\frac{d \ln D}{dT}$ has the value -0.005 for water we have

$$\Delta S = -V_{e1} \left(\frac{1}{T} + 0.005 \right) \quad (16)$$

The values of ΔS are given in the last column of table 10. The calculated values of ΔS correspond in sign and order of magnitude to those calculated from ΔF and ΔH values (8). This indicates that Gurney's (7) assumption of a temperature-independent factor (V_{non}) is valid.

SUMMARY

1. Relative acid strengths of carboxylic acids have been measured in the solvents water, methyl alcohol, ethyl alcohol, and water-dioxane mixtures.

2. It has been demonstrated that $\log K_{A_xB_0}$ is a linear function of $1/D$ between $D = 25$ and $D = 80$.

3. A comparison of the relative acid strengths in two solvents of equal dielectric constant showed that, for carboxylic acids, the relative strengths were the same.

4. Intrinsic acid strengths have been determined by extrapolation.

5. The entropies have been calculated from the relation between $K_{A_2B_0}$ and the dielectric constant.

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REFERENCES

- (1) ÅKERLÖF, G., AND SHORT, O. A.: J. Am. Chem. Soc. **58**, 1241 (1936).
- (2) BJERRUM, N., AND LUND, H.: Ber. **64B**, 210 (1931).
- (3) BROCKMAN, F., AND KILPATRICK, M.: J. Am. Chem. Soc. **56**, 1483 (1934).
- (4) BRÖNSTED, J. N.: Z. physik. Chem. **A169**, 52 (1934).
- (5) CHASE, E. F., AND KILPATRICK, M.: J. Am. Chem. Soc. **54**, 2284 (1932).
- (6) GOLDSCHMIDT, H.: Z. physik. Chem. **112**, 429 (1924).
- (7) GURNEY, R. W.: J. Chem. Phys. **6**, 499 (1938).
- (8) HAMMETT, L. P.: J. Chem. Phys. **4**, 613 (1936).
- (9) HAMMETT, L. P.: J. Am. Chem. Soc. **59**, 96 (1937).
- (10) KILPATRICK, M.: Trans. Electrochem. Soc. **72**, 95 (1937).
- (11) KOLTHOFF, I. M.: J. Phys. Chem. **35**, 1433 (1931).
- (12) LARSSON, E.: Dissertation, Lund, 1924. "Untersuchungen über die Elektrolytische Dissoziation einiger Electrolyte in Äthylalkoholische Lösung."
- (13) MASON, R. B., AND KILPATRICK, M.: J. Am. Chem. Soc. **59**, 572 (1937).
- (14) OSOL, A., AND KILPATRICK, M.: J. Am. Chem. Soc. **55**, 4430 (1933).
- (15) SAXTON, B., AND MEIER, H. F.: J. Am. Chem. Soc. **56**, 1918 (1934).
- (16) WYNNE-JONES, W. F. K.: Proc. Roy. Soc. (London) **A140**, 440 (1933).

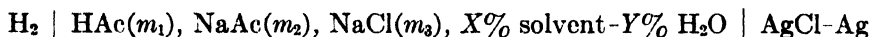
EXPERIMENTAL STUDIES OF THE IONIZATION OF ACETIC ACID¹

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From measurements of the electromotive forces of cells without liquid junction of the type



we have succeeded in obtaining accurate ionization constants of acetic acid in aqueous solution (3), in some methanol-water mixtures (5), and in 20, 45, and 70 per cent dioxane-water mixtures (6). These determinations were extended to cover a temperature range of from 0° to 50°C., so that they constitute the most extensive, accurate determination of an ionization constant of a weak electrolyte as a function of the temperature and of the dielectric constants of the solvent media.

The values of the ionization constant in dioxane-water mixtures determined by Harned and Kazanjian (6) were preliminary, and depended on standard potentials of the cells derived by the Debye and Hückel theory without the use of extended terms. These have been reevaluated (1, 2) by the more refined method, and final values of the ionization constant have been computed.

Because of the value of results of this kind as an experimental contribution to the statics and kinetics of ionization reactions, it seems appropriate to give a résumé of the final results and an estimation of their accuracy. In addition the heat content, the heat capacity, and the entropy of the reaction have been computed.

THE IONIZATION CONSTANT

Table 1 contains the revised values of the ionization constant K in dioxane-water mixtures containing 20 per cent, 45 per cent, and 70 per cent by weight of dioxane. No revision has been made of the values obtained by Harned and Ehlers (3) in water and by Harned and Embree (5) in methanol-water mixtures.

¹ Presented at the Symposium on Intermolecular Action, held at Brown University, Providence, Rhode Island, December 27-29, 1938, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society.

The absolute accuracy of these results is difficult to estimate, since uncertainties arise not only in the extrapolation which yields the required standard potential of the cell, but also in the extrapolation from which the ionization constant is obtained. At 25°C. an error of 0.1 millivolt in the extrapolated electromotive force corresponds to an error of 0.002 and 0.003 in $(-\log K)$, or an uncertainty of 0.5 to 0.7 per cent in the value of K . In aqueous solutions where the extrapolations are more certain,

TABLE 1

Ionization constant of acetic acid in dioxane-water mixtures

X = per cent of dioxane by weight; D = dielectric constant

t IN °C.	$X = 20$ PER CENT		$X = 45$ PER CENT		$X = 70$ PER CENT	
	D	$K \times 10^4$	D	$K \times 10^4$	D	$K \times 10^4$
0	69.2	4.75	44.3	4.78	20.4	4.75
5	67.4	4.87	43.0	4.89	19.8	4.83
10	65.7	4.98	41.9	4.96	19.2	4.89
15	64.0	5.05	40.7	4.96	18.7	4.83
20	62.4	5.09	39.6	4.96	18.2	4.83
25	60.8	5.11	38.5	4.93	17.7	4.78
30	59.9	5.08	37.4	4.86	17.2	4.69
35	57.7	5.03	36.4	4.75	16.7	4.56
40	56.3	4.95	35.4	4.61	16.3	4.42
45	54.8	4.86	34.4	4.44	15.8	4.22
50	53.4	4.73	33.4	4.28	15.4	4.05

TABLE 2

Parameters and constants of equation 1

SOLVENT	PER CENT BY WEIGHT OF METHANOL OR DIOXANE	LOG K_m	θ	LOG $K_m - p\theta^2$	$2p\theta$
Water.		5.2456	22.6	5.1945	0.00226
Water-methanol	10	5.0959	27.0	5.0585	0.00270
Water-methanol	20	5.9207	31.5	5.8710	0.00315
Water-dioxane.	20	5.7073	24.6	5.7073	0.00246
Water-dioxane.	45	7.6951	15.26	7.6951	0.001526
Water-dioxane.	70	9.6868	10.42	9.6868	0.001042

the error in the determination of K is of the order of ± 0.2 per cent. In the other solutions the error is estimated to be not less than ± 0.3 per cent and not more than ± 0.7 per cent. The uncertainty increases with decrease in the dielectric constant.

The experimental results may be expressed accurately by the simple equation of Harned and Embree (4), namely,

$$\log K = [\log K_m - p\theta^2] + 2p\theta t - pt^2 \quad (1)$$

where K_m is the value of K at its maximum, θ is the temperature at which K is a maximum, p has the value of $5 \times 10^{-5} \text{ deg.}^{-2}$, and t is the Centigrade temperature. Values of the parameters and constants of this equation are given in table 2. The maximum deviation between the observed values and those calculated by this equation is 0.004 in $\log K$ and occurs in the cases of media containing 45 per cent and 70 per cent of dioxane. The average deviation is 0.002 or less. This is approximately the estimated accuracy of the experimental values.

HEAT CONTENT, HEAT CAPACITY, AND ENTROPY CHANGES

The changes in heat content and heat capacity accompanying the reaction are given by the equations

$$\Delta H = -4.575 \times 10^{-4} T^2 (t - \theta) \quad (2)$$

$$\Delta C_p = -4.575 \times 10^{-4} T (T + 2 (t - \theta)) \quad (3)$$

derived by the differentiation of equation 1. The changes in free energy and subsequently in the entropy may be obtained from the customary fundamental thermodynamic relations,

$$\Delta F = -2.3026 RT \log K \quad (4)$$

$$\Delta S = -\frac{\Delta F - \Delta H}{T} \quad (5)$$

Values of these quantities at 25°C. are given in table 3.

TABLE 3
Free energy, heat content, heat capacities, and entropy changes at 25°C.

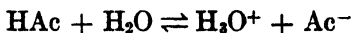
SOLVENT	PER CENT BY WEIGHT OF METH- ANOL OR DIOXANE	D	ΔF	ΔH	$(-\Delta C_p)$	$(-\Delta S)$
			<i>calories</i>	<i>calories</i>	<i>calories</i>	<i>calories</i>
Water.		78.5	6486	-98	41.3	22.1
Water-methanol	10	74.0	6690	81	40.1	22.2
Water-methanol	20	69.2	6930	264	38.9	22.4
Water-dioxane	20	60.8	7216	-16	40.8	24.3
Water-dioxane.	45	38.5	8600	-394	43.3	30.2
Water-dioxane	70	17.7	11347	-594	44.6	40.1

The determination of ΔF is accurate and the error in its estimation is less than 0.1 per cent. Owing to the difficulties of determining a quantity by differentiation, the values of ΔH are subject to a large error, estimated to be of the order of 100 cal. It is possible that by using the same function (equations 1 and 2) the relative error is less than this. In any case, the

increase in ΔH with increasing alcoholic content and the decrease with dioxane content of the solvent have a real significance. The error in ΔS is determined by the error in ΔH and amounts to approximately 0.3 cal. The absolute value of $(-\Delta C_p)$ is probably known within ± 3 cal., but the relative error is less than this, and the tendency of this quantity to decrease in the alcoholic solutions and to increase in the dioxane solutions is real. The temperature, θ , at which the maximum of K occurs is known within 2°C . in all cases, and probably within a narrower limit than this in most cases. These estimates are approximations designed to show how much confidence may be placed in these results. This method of computation gives the best results in the middle temperature range and should be reliable from 10° to 40°C .

VARIATION OF IONIZATION CONSTANTS WITH MACROSCOPIC DIELECTRIC CONSTANT

This method measures the sum of the concentration of free protons, hydronium ions, and solvated protons which we represent by m_{H} . The principal reaction is certainly



since even in the 70 per cent dioxane mixtures the mole fraction of water is of the order of 0.7. Evidence for this conclusion may be derived from the studies of hydrochloric acid in these mixtures both by conductance and by electromotive forces. The latter may be computed by the extended Debye and Hückel theory by employing the same mean distance of approach of the ions, a , at all temperatures from 0° to 50°C . in 70 per cent dioxane solution as in water (2). Conductance measurements give, according to Bjerrum's theory of ionic association, a value for " a " of 6\AA . in 82 per cent dioxane mixtures, whereas 5.6\AA . fitted the electromotive force measurements in the 70 per cent solutions. This is not direct evidence, but it shows that the results may be computed on the assumption that the same species of solvated ion is predominant in all the media. Transference number data may help to elucidate this question.

In figure 1, $\log K - \log K_0$ has been plotted against the reciprocal of the dielectric constant. K_0 and K are the values of the ionization constant in pure water and in the water-solvent mixtures, respectively. The lower curve represents the variation of the ionization constant of acetic acid, $(m_{\text{H}}m_{\text{Ac}}/m_{\text{HAc}})_{\mu=0}$ in dioxane-water mixtures (circles). Values of this quantity in methyl alcohol-water mixtures are indicated by crosses within squares. For purposes of comparison, $\log K_0 - \log K$ (derived from recent results²) of the ionization constant of water, $m_{\text{H}}m_{\text{OH}}/a_{\text{H}_2\text{O}}$ pure solvent,

² Measurements of suitable cells by Mr. Leslie Fallon in this laboratory.

is shown in the middle curve. The top curve is a similar plot for $m_H m_{OH} N_{H_2O} / a_{H_2O}$ pure solvent, where N_{H_2O} is the mole fraction of water. This quantity may be used as a rough estimate of $m_H m_{OH}$.

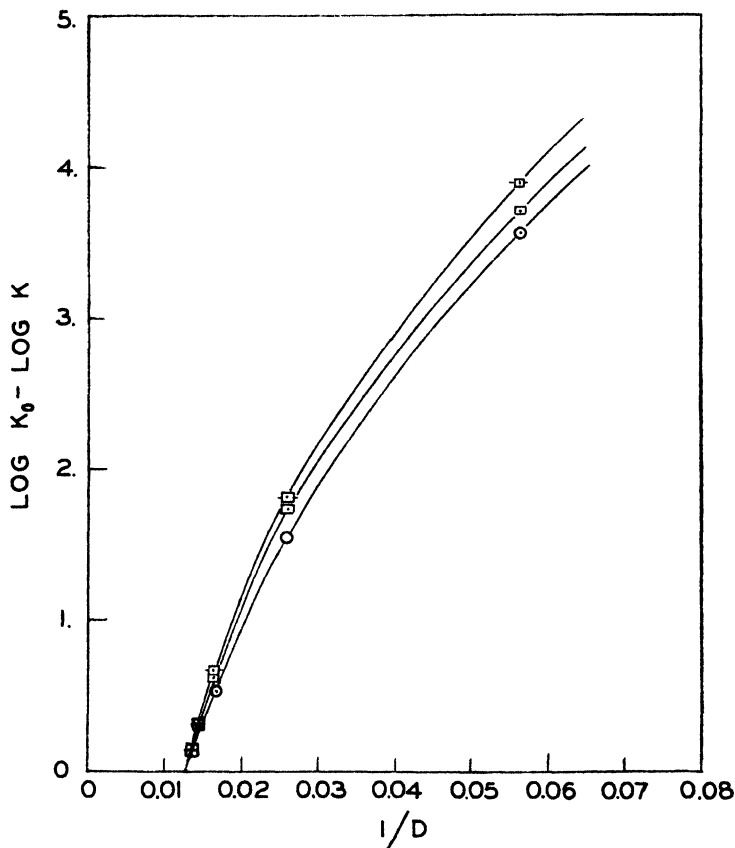


FIG. 1. Plots of $\log K_0 - \log K$ versus $1/D$

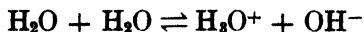
$$\left. \frac{m_H m_{Ac}}{m_{HAc}} \right]_{\mu=0} \quad \text{in dioxane-water mixtures}$$

$$\left. \frac{m_H m_{Ac}}{m_{HAc}} \right]_{\mu=0} \quad \text{in methanol-water mixtures}$$

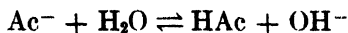
$$\left. \frac{m_H m_{OH}}{a_{H_2O}} \right]_{\text{pure solvent}} \quad \text{in dioxane-water mixtures}$$

$$\left. \frac{m_H m_{OH} N_{H_2O}}{a_{H_2O}} \right]_{\text{pure solvent}} \quad \text{in dioxane-water mixtures}$$

There are a few conclusions apparent from this plot: (1) The plots possess a distinct curvature. (2) The extent of the variation of the ionization constant of water is of the same order of magnitude as the variation of the ionization constant of the acid. On the other hand, since the scale of the figure is not large, the difference is considerable and may be measured accurately. The reaction for the water ionization may be assumed to be



so that the difference between the water and acetic acid curves corresponds to the variation in the logarithm of the equilibrium constant of the hydrolysis reaction,



SUMMARY

1. Revised values of the ionization constant of acetic acid in dioxane-water mixtures have been tabulated. The probable accuracy of the results has been estimated.

2. The results have been expressed as a function of the temperature by the approximate equation

$$\log K - \log K_m = p(t - \theta)^2 \quad (1)$$

and the parameters K_m and θ have been tabulated.

3. Values of ΔH , ΔC_p , and ΔS of the ionization reaction at 25°C. have been tabulated. The probable errors of their determination have been estimated.

4. The variation of the logarithm of the ionization constant with the reciprocal of the dielectric constant has been discussed and contrasted with a similar variation of the ionization constant of water.

REFERENCES

- (1) HARNED: J. Am. Chem. Soc. **60**, 336 (1938).
- (2) HARNED AND CALMON: J. Am. Chem. Soc. **60**, 2130 (1938).
- (3) HARNED AND EHLERS: J. Am. Chem. Soc. **54**, 1350 (1932); **55**, 652 (1933).
- (4) HARNED AND EMBREE: J. Am. Chem. Soc. **56**, 1050 (1934).
- (5) HARNED AND EMBREE: J. Am. Chem. Soc. **57**, 1669 (1935).
- (6) HARNED AND KAZANJIAN: J. Am. Chem. Soc. **58**, 1812 (1936).

DISCUSSION OF THE PAPERS PRESENTED AT THE SYMPOSIUM ON INTERMOLECULAR ACTION¹

Intermolecular Forces and the Properties of Gases (page 15). J. O. HIRSCHFELDER AND W. E. ROSEVEARE (University of Wisconsin).

J. H. HILDEBRAND (University of California): I should like to comment on several items in this unusually interesting contribution. First, I agree that liquid butane should show evidence of hindered rotation in the liquid phase. I think that I shall be able to show the presence of structure in non-associated liquids such as this by examination of the small departures from my rule regarding entropy of vaporization.

Second, someone could perform a service by getting accurate measurements of $(\partial p/\partial T)_v$ for vapors of some of the tetrahalides for which we already have such data for the liquids.

Third, I have quite recently secured evidence of an altogether different sort regarding the change in the slope of the energy *versus* density lines. This is being published in a forthcoming issue of the Journal of Chemical Physics. Briefly, it indicates that the "constant" a in the equation

$$\partial E/\partial V = a/V^2$$

falls off by several per cent while a liquid expands through a rather long temperature interval. This effect may prove to be uniform for all normal symmetrical molecules, which will make it extraordinarily useful.

Fourth, I believe that in changing from liquid to vapor the a will fall off appreciably, owing to the change in the distribution function, $W(r)$. I think that for a gas this is somewhat different from the form given in figure 8 (page 33). The peak for the liquid is due to the interference of the central molecule, on one side, and the molecules of the second rough layer on the other. The latter are absent in the gas and all positions have unit probability except very close to the central atom where the attractive force causes acceleration, diminishing the time spent and causing a downward bending of the function.

¹ This Symposium on Intermolecular Action was the third annual symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society. It was held at Brown University, Providence, Rhode Island, December 27-29, 1938.

Only comments received in written form are included in this discussion. The officers of the Division are not responsible for any of the opinions expressed.

The page numbers given refer to Volume 43 of This Journal, unless otherwise noted.

G. SCATCHARD (Massachusetts Institute of Technology): With the possible exception of measurements at very low pressures, the severest test of any equation of state is the p - V - T relationship itself. The energy is a less satisfactory criterion, particularly near the extreme of the experimental temperature range. If the energy is a linear function of the density, the change with temperature of

$$V(pV/RT - 1) = B' + C'/V + D'/V^2 + \dots$$

is independent of the density. Examination of the experimental data shows, however, that, for water between 440° and 460°C., the contribution of C' , D' , etc. varies more than B' does. The same is true for carbon dioxide at 125° and 150°C. only up to a density of 100 Amagat units. These results may mean merely that the material for comparison was not well chosen, and that experimental measurements have not been carried to a really "high temperature" for either of these substances.

The Liquid State (page 37). JOHN F. KINCAID (University of Rochester) AND HENRY EYRING (Princeton University).

W. H. RODEBUSH (University of Illinois): The concept of communal entropy as introduced by Dr. Eyring and his colleagues implies a difference in entropy which amounts in the limit to R units between gases at N.T.P. and crystalline solids. Liquids presumably acquire this entropy at higher temperatures. It is, of course, easily demonstrated from the Bose-Einstein statistics that the process of partitioning the space occupied by a gas in cells of equal volume with each cell occupied by one molecule would decrease the entropy by R units. While the process involved in this partitioning is physically impossible, there is no objection to discussing the abstract case.

On the other hand, one may pass from this example to an example of an ideal crystal by supposing the molecules to be transformed into harmonic oscillators without any interaction. The entropy of such a system of oscillators is given by the Einstein expression, and it will be seen at once that it is less by R units than the value given by the Debye formula for an actual monatomic lattice. It follows, therefore, by this argument that all forms of matter—solid, liquid, and gaseous—must acquire this so-called communal entropy at higher temperatures.

As a matter of fact, the R units of entropy are seen not to depend upon a free volume but rather to involve the question of whether the wave function is limited to the volume occupied by the molecule or not. For example, in the hypothetical model of gas or crystal the wave function is bounded by the walls of the partition, while for an actual gas the wave function has a value throughout the whole volume occupied by the gas, and for the exact description of a real crystal the wave function must be

written for the crystal as a whole. The behavior of liquids will be commented on in connection with the next paper.

J. H. HILDEBRAND (University of California): In my forthcoming paper referred to in my comments on the paper of Dr. Hirschfelder and Dr. Roseveare, I give evidence, somewhat to my own surprise, that mercury, in spite of its metallic character, can properly serve as an illustration of a normal liquid in the manner used by Dr. Kincaid and Dr. Eyring.

The State of Liquid Helium near Absolute Zero (page 49). F. LONDON (University of Paris).

W. H. RODEBUSH (University of Illinois): The discussion of liquid helium by Dr. London is extremely interesting. Some years ago I called attention to the fact that the entropy of liquid helium might be reduced to zero, even though the liquid were in completely unordered state (J. Chem. Phys. **2**, 668 (1934); Phys. Rev. **47**, 513 (1935)). In arriving at this conclusion I assumed that the liquid mass acted as a single molecule and that a single wave function could be written for the whole number of atoms in a manner analogous at least to the treatment of electrons in a metal.

The Bose-Einstein statistics must be used, of course, and I suggested that, since the number of configurations was not large and the potential barriers between configurations low, the multiplet separation might be considerable, and thus that liquid helium might reach the lowest energy state at finite temperatures giving, of course, zero entropy, with an entirely random and constantly shifting arrangement of molecules in the liquid. The striking fact of superfluidity lends strong support to this idea. If at the lowest energy level one configuration of helium molecules may flow into another without traversing a high potential barrier, so that the multiplet separation is considerable but the energies are limited to a narrow band, one would, of course, expect a very erratic behavior of the specific heat curve. The entropy would, of course, be zero when the system is in the lowest energy state. Furthermore, the resonance between the various configurations might contribute appreciably to the stabilization of the liquid phase relative to the crystal.

Order and Disorder in Liquid Solutions (page 97). JOHN G. KIRKWOOD (Cornell University).

J. H. HILDEBRAND (University of California): Dr. Kirkwood need not apologize for dealing with a problem of only theoretical interest as there are, actually, a number of non-polar components forming two liquid phases. Foreseeing the interest in this kind of problem, I have discovered a number of such systems, including iodine with carbon tetrachloride, stannic iodide with silicon chloride and with various paraffins, phosphorus with carbon

disulfide and other substances. I hope that Dr. Kirkwood and others will play with these systems.

It has been my thought that light should be thrown on the extent of clustering by discrepancies existing near the consolute temperature between the actual solubility curves and curves calculated with neglect of the clustering effect.

G. SCATCHARD (Massachusetts Institute of Technology): It will doubtless be very difficult to check experimentally the theory of Dr. Kirkwood's paper, especially from the mutual solubility. The calculated free energy of the mixture differs from that of a regular solution in two ways. At constant temperature the free energy *versus* mole fraction curve is flatter, and at constant composition the excess free energy increases with increasing temperature. The first effect tends to flatten the solubility *versus* temperature curve and the second tends to make it less flat, so that the two tend to compensate. I believe the most important result of such calculations is the conclusion, reached by both Dr. Kirkwood and Rushbrooke, and now by Guggenheim (Proc. Roy. Soc. (London) **A169**, 134 (1938)), that the effect of order is very small for spherical molecules even at the consolute temperature.

Several Solutions of Non-polar Substances (page 109). J. H. HILDEBRAND (University of California).

J. H. HILDEBRAND (University of California): The results referred to in the footnote on page 113 have been obtained and are published on page 299 of this issue.

PAUL GROSS (Duke University): The hypothetical case considered by Fowler and Rushbrooke and quoted by Dr. Hildebrand, of two components, the molecules of one of which occupy one point each in a lattice, while the molecules of the other occupy two adjacent lattice points, is realized about as well as can be hoped for by the system benzene-diphenyl. Recently Dr. Gilmann and I published determinations at a number of temperatures of the partial pressure of benzene from its solutions with diphenyl (J. Am. Chem. Soc. **60**, 1525 (1938)). With the method employed it was possible to make determinations only from 0.7 to 1.0 mole fraction of benzene. In this region, however, Raoult's law for pressures was obeyed closely. It is of interest to note that this is the region where Fowler and Rushbrooke find a practically linear relation between the partial vapor density of the single molecules and their mole fraction.

G. SCATCHARD (Massachusetts Institute of Technology): Although I should like to discuss each part of Professor Hildebrand's very interesting paper, time will permit only calling attention to one very different treatment of long-chain hydrocarbons. Berger (Rec. trav. chim. **57**, 1029 (1938)) has very recently measured the boiling point elevation

of solutions of long-chain hydrocarbons in *n*-hexane, as well as in cyclohexane and in benzene. He finds positive deviations from Raoult's law with *n*-hexane when the number of carbons in the solute molecule is less than sixteen, and negative deviations when there are more than sixteen carbon atoms. It is interesting to compare his picture of such solutions with that of Professor Hildebrand, for he believes that the long-chain hydrocarbons are so coiled that there are parts of their surfaces that cannot make contact with another long-chain hydrocarbon, although they can be reached by the smaller hexane molecules. My computations indicate that it would be sufficient to account for the effect of the longest chains he studied, which contained thirty-one and thirty-three carbon atoms, if one five-hundredth of the surface were so sheltered.

The Effect of Intermolecular Action upon Dielectric Polarization (page 131).

CHARLES P. SMYTH (Princeton University).

J. G. KIRKWOOD (Cornell University): It seems likely that the Onsager calculation of the local field in polar dielectrics and the Debye theory of hindered rotation may have a common physical background. The departure of the local polarization from its average value near a dipole molecule, implicit in the Onsager theory, involves correlation of the orientations of the central dipole and those constituting the medium. This is a form of hindered rotation due to the electrostatic interaction. The Debye theory, on the other hand, takes account, in an empirical manner, of hindered rotation due to all intermolecular forces. Electrostatic forces probably constitute an important part, if not the dominant part, of the interaction responsible for hindered rotation.

The Problem of Free Rotation in Complex Dipolar Ions in Solution (page 143). JEFFRIES WYMAN, JR. (Harvard University).

J. WYMAN, JR. (Harvard University): In reading the preprint I note two errors which were passed over in the proof. In the first place, the numerical values listed for \bar{C}^2/nC_1^2 on page 146 are in reality values for the square root of this quantity. The correct values for \bar{C}^2/nC_1^2 are: $n = 2$, 1.33; $n = 3$, 1.52; $n = 4$, 1.63; $n = 10$, 1.85; $n \rightarrow \infty$, 2. In the second place, the second sentence on page 147 should read: "For this case . . . the values obtained for \bar{C}^2 . . . increase somewhat *more* rapidly than in proportion to n ."

The Apparent and Partial Molal Heat Capacities and Volumes of Glycine and Glycolamide (page 153). FRANK T. GUCKER, JR., WILLIAM L. FORD, AND CHARLES E. MOSER (Northwestern University).

J. H. HILDEBRAND (University of California): It may not be out of place to utter here a few words intended not in any way as a criticism

of the paper under discussion but as a general caution to workers with such systems. The partial derivative of any extensive property of a binary solution with respect to the number of moles of one component is defined as the partial molal property of that component. Its magnitude, however, may depend largely on what happens to the other component. For example, when the partial molal volume of a salt in aqueous solution is negative it is mainly the change in water structure that is responsible.

Studies in the Physical Chemistry of Amino Acids, Peptides, and Related Substances. XII. Interactions between Dipolar Ions in Aqueous Solution (page 169). EDWIN J. COHN, T. L. McMEEKIN, JOHN D. FERRY, AND MURIEL H. BLANCHARD (Harvard Medical School). (Also preceding paper.)

R. M. Fuoss (General Electric Company): The preliminary theory of dipole-dipole interaction (R. M. Fuoss: J. Am. Chem. Soc. **56**, 1027 (1934); **58**, 982 (1936)) contains several physical and mathematical approximations, which limit its generality. The parameter which appears as the independent variable contains the ratio (μ^2/Da^3) , where μ is the dipole moment (μ^* of Onsager's theory), a is a diameter of the dipole molecule, and D is the dielectric constant of the solvent, assumed to be a homogeneous continuum. Several models for the dipole molecule were used, but both assumed *point* dipoles at the center. Considerable improvement, for comparison with the data of Professor Gucker and of Professor Cohn, can be expected by replacing the point dipole model with a model in which the dipole consists of discretely separated charges. The rough agreement found by the above authors between their experimental data and the slopes predicted by the theory is undoubtedly due to a compensation of approximations in the theory; the theory was originally developed for the case of solvents of low dielectric constant, such as benzene, but the large moments of the amino acids compensate to a large extent for the large dielectric constant of water in calculating the parameter (μ^2/Da^3) .

The agreement is actually better than appears at first sight, because both authors used *independent* values of μ and a in their calculations, and in work of this sort the parameter a is usually left as an arbitrary constant to be derived from the data. When the physical approximations are considered, it does not seem unreasonable to expect different a values to be obtained from different kinds of data, because the differences between model and molecule appear in different ways in electrical, hydrodynamic, and thermodynamic properties.

The approximation of the solvent as a continuum, described electrically solely by its macroscopic dielectric constant D , could be improved by using a dielectric constant $D(r)$ which was a function of the distance r from an ion or dipole molecule. A solvent molecule near an ion or strong

dipole cannot rotate at all in the external field, and even the electronic polarization is saturated. Near an electrical singularity, therefore, the effective dielectric constant is unity. At a distance r_0 , given by $\mu\epsilon/r_0^2 DkT = 1$, from an ion, a dipole has an equal chance of being oriented by the central ion or assuming a random orientation. In this range of distances the dielectric constant is approximately n^2 , the square of the index of refraction. For very large distances $D(r)$ becomes the macroscopic dielectric constant. We therefore expect that $D(r)$ will be an S -function, starting at $D(a/2) = 1$ and approaching $D(\infty) = D$. This function can be approximated by a step function:

$$D(r) = 1, a/2 \leq r \leq ma$$

$$D(r) = n^2, ma \leq r \leq r_0$$

$$D(r) = D, r_0 \leq r \leq \infty$$

where m is a small number, so that ma equals the radius of the central molecule plus the thickness of several layers of solvent molecules.

G. SCATCHARD (Massachusetts Institute of Technology): The insufficiency of a dipole of infinitesimal length, but finite moment, at the center of a sphere for the representation of the positions of charges in a molecule, to which Dr. Fuoss has called attention, is especially marked in those substances to which "hydrogen bonds" have been attributed, because in them the protonic charge is so near the surface of the molecule. There is reason to suppose that most of the interaction is electrostatic even between hydroxyl radicals. The change in infrared frequency indicates that the distribution of charges is altered by the presence of the "acceptor," but gives no evidence that the interaction energy is greatly changed thereby.

Pressure-Volume-Temperature Relations in Solutions. I. Observations on the Behavior of Solutions of Benzene and Some of its Derivatives (page 207).

R. E. GIBSON AND O. H. LOEFFLER (Geophysical Laboratory, Carnegie Institution of Washington).

J. H. HILDEBRAND (University of California): I should like to make a comment on the Tait equation. Of its use to correlate these well-chosen and evidently accurate data I have not the slightest criticism, but it has a form whose theoretical significance is not easy to see. It deals with increments rather than differentials, and it adds one more to the already rather baffling list of internal pressures. It uses $p + B$. What is the relation of B to the terms in the thermodynamic equations of state, such as,

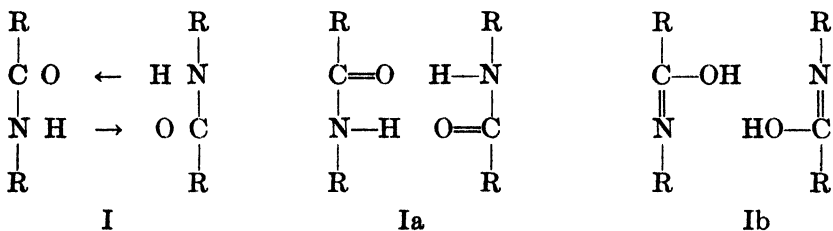
$$p + (\partial E / \partial V)_T = T(\partial p / \partial T)_* = T(\partial S / \partial V)_T$$

Dr. Gibson could help us by touching upon such relationships.

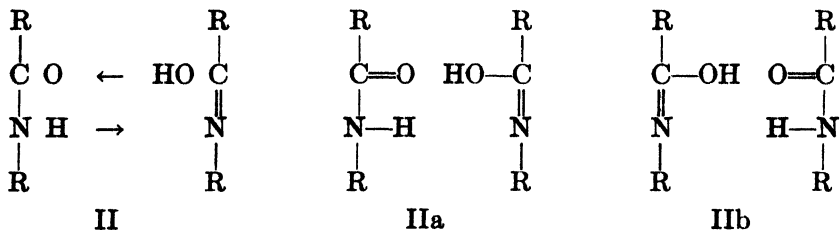
R. E. GIBSON (Carnegie Institution of Washington): The relations requested by Professor Hildebrand are discussed in a paper with Dr. Kincaid (J. Am. Chem. Soc. **60**, 511 (1938)).

Association through Hydrogen (page 219). W. H. RODEBUSH AND A. M. BUSWELL (University of Illinois).

L. MICHAELIS (Rockefeller Institute for Medical Research): The formation of a hydrogen bond has attained a great importance in the theory of the structure of proteins. A first attempt to formulate such bonds would be formula I. This would involve a resonance between Ia and Ib.



Ia is a ketonic structure, Ib an enolic one. The first is much more favored in a peptide group. Ia and Ib would be two arrangements of very different stability, so there cannot be any appreciable resonance, or, in other words, there can be no appreciable hydrogen bond. However, another formulation would be II, which would mean resonance between IIa and IIb.



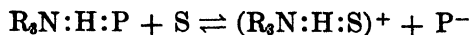
Here each limiting state (IIa or IIb) shows the enol structure, which of its own account should be not very stable. However, in the combination of both limiting states IIa and IIb, which are symmetric to each other, there should be strong resonance; in other words, there should be a hydrogen bond. So I propose the hydrogen bond for peptide structures such as II. This formulation gives an entirely different aspect of the hydrogen bond in peptides, which may have a very essential bearing for consideration of protein structures.

Non-Coulombic Interactions in Solutions of Electrolytes (page 231).

CHARLES A. KRAUS (Brown University).

M. KILPATRICK (University of Pennsylvania): The results with partially

substituted ammonium salts indicate that these compounds exist to some extent in the form of non-ionic molecules. In aprotic solvents, such as nitrobenzene and ethylene chloride, the extent of non-ionic molecule formation might be expected to increase with increasing basic strength of the anion. Thus for the same cation the picrate would always give a lower dissociation constant than the perchlorate. In a basic solvent such as pyridine the solvent plays a rôle and we may write



which will make the dissociation constant less dependent on the anion.

Considering a series of salts with the same anion in aprotic solvents the extent of non-ionic molecule formation would show some correlation with the acid strength of the cation. These acid strengths will vary with the solvent. The leveling effect of a basic medium is again illustrated in the last column of table 2 (page 237).

KASIMIR FAJANS (University of Michigan): For the explanation of the important results obtained by Professor Kraus some points of view may be of interest, which have proved to be of value in different lines of research pursued by my collaborators and myself in the last fifteen years (*Naturwissenschaften* **11**, 165 (1923); *Z. Krist.* **66**, 18 (1925)). We know now that in considering the non-Coulombic interaction between ions as well in solution as in the more simple cases of a gaseous molecule or a crystal lattice, the following factors must be taken into account besides the potential of repulsion: the mutual polarization of ions, the wave mechanical exchange energy, and the van der Waals' attraction. The quantitative treatment is obviously very complex. But for qualitative understanding of numerical relations the problem can be simplified considerably. So in the case of simple, inorganic ions the polarization of the anion in the field of the cation predominates over the opposite effect (*Z. Elektrochem.* **34**, 502 (1928)). But the stronger the polarization of the anion, the more its electronic shell is pulled toward the cation, the less the polarity of the compound, and the more does it approach the covalent type of binding. In general, the share of the wave mechanical covalent exchange energy will go parallel with the polarization of the anion. On the other hand, the van der Waals' attraction, as F. London has shown, depends also upon the polarizability of the particles involved. Thus it is understandable why the polarizability of ions and molecules and their polarizing ability proved to be such important factors in the explanation of numerous properties of inorganic substances and their aqueous solutions; specifically of properties due to non-Coulombic interaction, summarized under the term "deformation" of ions and molecules.

The organic substances dealt with in the paper of Professor Kraus are more complicated, and it is more difficult to estimate the rôle of different factors, but some of the results can be shown to be closely related to those

found in the cases of simpler compounds. It is stated that, in nitrobenzene as solvent, hydrochloric acid is a weak electrolyte, whereas perchloric acid is strong, and that the dissociation constant of butylammonium perchlorate is higher than that of the picrate. In ethylene chloride the pyridonium perchlorate is a stronger electrolyte than the picrate. All of these facts are undoubtedly connected with the small polarizability of the perchlorate ion. Its measure is the molar refraction (3.4 cc.) of one oxygen octet of the perchlorate ion, which is considerably smaller than the refraction of the chloride ion (9 cc.). It is difficult to give an exact value for the polarizability of that part of the complex picrate ion which is involved in the association of the cation with it, but this value is certainly larger than the polarizability of the perchlorate ion. The effect of the deformation of the anion upon the degree of dissociation of the electrolyte is the same as has been pointed out by Professor Kraus for the quantum forces and is obviously analogous to that which has been discussed in detail for the case of solubility (Z. Krist. **66**, 18 (1925)). The energy of solvation of the free ions has to be overcome, besides the Coulombic attraction, also the energy of deformation (polarization, the covalent exchange energy, etc.).

Of great interest is the decreasing effect of the protons contained in the cation on the dissociation constant of the electrolyte. An analogous effect was found in the study of the change with concentration of the molar refraction of ammonium salts and strong acids in aqueous solutions (Z. physik. Chem. **137**, 361 (1928)). This change is considered as the refractometric evidence of the association of ions, and its strength shows, in the case of numerous strong electrolytes, a gradation which can be understood from the point of view of the properties of the ions involved. But in the case of the ammonium salts and strong acids the refractometric effect was stronger than expected. It was necessary to assume that here the association of the ions is connected with a shift of the protons inside the NH_4^+ or OH_3^+ towards the anion. This shift of the protons is accompanied by an increase of the polarizing effect of the cation on the anion and probably of the exchange energy of their binding. This gives, at least for these cases, a picture of that which is called "the hydrogen bond."

Ion Conductances in Water-Methanol Mixtures (page 239). L. G. LONGSWORTH AND D. A. MACINNES (Rockefeller Institute for Medical Research).

G. SCATCHARD (Massachusetts Institute of Technology): Since the change of mobility with changing solvent is approximately the same for three ions as different as Li^+ , Na^+ , and Cl^- , it seems difficult to attribute this change to solvation. If the viscosity for all particles of atomic dimensions differs from the macroscopic viscosity to about the same extent, these measurements would be explained. The measurement of transfer-

ence with polyvalent ions and of the diffusion of neutral molecules should yield interesting information.

Thermodynamics of Strong Electrolytes in Protium Oxide-Deuterium Oxide Mixtures. I. Hydrogen Chloride (page 247). EVAN NOONAN AND VICTOR K. LAMER (Columbia University).

H. C. UREY (Columbia University): The very careful work that has been done by Professor LaMer and his colleagues has given us very exact data on the behavior of electrolytic solutions in protium and deuterium oxides and their mixtures, as well as a better understanding of the kinetics of reactions in these solutions. In this paper Dr. Noonan and Professor LaMer have made very precise measurements on the electropotential of a simple cell. I only wish to give, in brief, the results of some calculations relating to the very interesting maximum in the $E_0 - E_n$ curve as a function of the mole fraction of deuterium in the solution. The potential of this cell can be written in the following form:

$$E_n = E_0^0 - \frac{RT}{F} \ln \frac{[H_3O^+][Cl^-]}{P_{H_2}^{\frac{1}{2}}[H_2O]} \quad (1)$$

where the symbols have their usual significance and where the H_2O is included in the expression within the logarithm, since its concentration changes with the composition of the water. As a first approximation we make the assumption that the constant E_0^0 does not change with the mole fraction of deuterium in the water, and if this is true expression 1 gives the value for the potential for all compositions of the water and the gas providing we use the activity of H_3O , the partial pressure of the H_2 , and the mole fraction of H_2O . These can be calculated for a given value of the mole fraction of deuterium in the water in the terms of six equilibrium equations and four additional equations, as follows:



$$P_{H_2} + P_{HD} + P_{D_2} = P$$

$$[H_2O] + [HDO] + [D_2O] = 1$$

$$[H_3O^+] + [H_2DO^+] + [HD_2O^+] + [D_3O^+] = [Cl^-]$$

$$\frac{2[D_2O] + [HDO]}{2} = \alpha$$

The K 's are the equilibrium constants of the corresponding expressions, and α is the measured mole fraction of deuterium in the water, if the amount of oxonium ion can be neglected relative to the water.

The calculations are straightforward but tedious. The following equation gives the result of these calculations:

$$E_n = E_0 - \frac{RT}{F} \ln \frac{[\text{Cl}^-]^2}{P^{\frac{1}{2}}} - \frac{RT}{F} \ln \left[\frac{K_3^2 r^4 - K_1 K_3 r^2 + 2K_3 r^2 + 1}{K_3 r^2 + 1 - \sqrt{K_1 K_3} r} \right]^{\frac{1}{2}} \frac{1}{1 + K_4^{\frac{1}{2}} K_6^{\frac{1}{2}} r + K_6^{\frac{1}{2}} K_8^{\frac{1}{2}} r^2 + K_6^{\frac{1}{2}} r^3} \cdot \frac{1}{[\text{H}_2\text{O}]}$$

where r is defined as the square root of the ratio of the $[\text{D}_2\text{O}]$ to the $[\text{H}_2\text{O}]$ in the water, and is given by the equation,

$$r = \left\{ \frac{8\alpha + K_2 - 2K_2^2\alpha - [K_2^2 + 4K_2(4 - K_2)\alpha - 4K_2(4 - K_2)\alpha^2]^{\frac{1}{2}}}{8 - 8\alpha - K_2 + 2K_2\alpha - [K_2^2 + 4K_2(4 - K_2)\alpha - 4K_2(4 - K_2)\alpha^2]^{\frac{1}{2}}} \right\}^{\frac{1}{2}}$$

while the mole fraction of H_2O is given by the expression,

$$[\text{H}_2\text{O}] = \frac{8 - 8\alpha - K_2 + 2\alpha K_2 - [K_2^2 + 4K_2(4 - K_2)\alpha - 4K_2(K_2 - 4)\alpha^2]^{\frac{1}{2}}}{2(4 - K_2)}$$

I have expanded this long and involved expression in terms of the mole fraction, α , in the region where α is small and also in terms of β , the mole fraction of hydrogen in the water, in the region where β is small. This gives the following two equations for these two cases, respectively:

$$E_n = E_0 - \frac{RT}{F} \ln \frac{[\text{Cl}^-]^2}{P^{\frac{1}{2}}} - \frac{RT}{F} \left[\frac{K_1^{\frac{1}{2}} K_3^{\frac{1}{2}}}{K_2^{\frac{1}{2}}} + 2 - 2 \frac{K_1^{\frac{1}{2}} K_6^{\frac{1}{2}}}{K_2^{\frac{1}{2}}} \right] \alpha$$

$$E_n = E_0 - \frac{RT}{F} \ln \frac{[\text{Cl}^-]^2}{P^{\frac{1}{2}}} - \frac{RT}{F} \left[\frac{K_1^{\frac{1}{2}}}{K_2^{\frac{1}{2}} K_3^{\frac{1}{2}}} + 2 - 2 \frac{K_6^{\frac{1}{2}}}{K_2^{\frac{1}{2}} K_3^{\frac{1}{2}}} \right] \beta - \frac{RT}{2F} \ln \frac{K_3}{K_6}$$

The values of E_0 and E_1 for pure protium oxide and deuterium oxide, respectively, are given by these expressions by setting α and β equal to zero.

The experimental value of Noonan and LaMer for $E_0 - E_1$ enables us to calculate the constant K_6 in terms of K_3 , which is known from theoretical calculations to have the value 1/9.3. This calculation gives the value of $K_6 = 0.07593$. It is easily seen that the slopes of the curve given by Noonan and LaMer are given by the quantities multiplying α and β of these expressions. I have taken the slope of the curve in the region of the small α to be 11.9 millivolts, while the slope in the region of small β I have taken as 10.5 millivolts. In this way it is possible to calculate

K_4 and K_5 , since the values of K_1 , K_2 , K_3 , and now K_6 , are known. The result of the calculation gives $K_4^{1/3}$ equals 2.652 and $K_5^{1/3}$ equals 2.794. Using these values of the constants I have calculated the potential at $\alpha = 0.75$ and have secured the value 5.22 millivolts, instead of 6.0 millivolts as given by Noonan and LaMer. My experience with the calculation shows that rather small changes in the constants would account for the discrepancy, though time has not permitted the calculation of the complete curve. It is quite evident that if the constants can be chosen to give the slopes of these curves at the two limits, the remainder of the curve will at least follow closely the curve given by these authors.

The simple statistical values for $K_4^{1/3}$ and $K_5^{1/3}$ would be 3 in each case, and thus the values calculated for these constants are certainly reasonable in view of our experience with exchange reactions of this sort. Thus the constants K_1 and K_2 have the values 3.26 and 3.27 instead of the simple statistical value of 4. This would lead us to expect, perhaps, that the constants K_4 and K_5 should be slightly less than the simple statistical values, which is the case.

Of course, our experience with the vapor pressures of the varieties of water, the solubilities of salts in water, and similar phenomena, show that one can expect that the normal potential E_0^0 , as given in equation 1, will not remain exactly constant over the whole range. If one assumes that it is necessary to add a linear term in the mole fraction, say $K\alpha$, to equation 1, and that this term is sufficient to account for the entire difference 4.47 observed by Noonan and LaMer, some changes in the calculated constants result. In the first place, K_6 becomes equal to K_3 and the slope of the curve in the region in which α is small must be decreased by 4.47, while the slope in the neighborhood of small β must be increased by the same amount. This changes the entire equation and gives $K_6 = 1/9.3$, $K_4^{1/3} = 3.45$, and $K_5^{1/3} = 3.59$. Our experience with exchange reactions between different isotopic varieties of the same chemical substance leads us to expect that the constants $K_4^{1/3}$ and $K_5^{1/3}$ will be less than 3 rather than greater than 3, and hence that no very great change in the calculation can be made in the direction indicated in this paragraph. Probably for most calculations the constants $K_4^{1/3}$ and $K_5^{1/3}$ can be taken as equal to 3 without serious error.

Similar calculations have been made by Schwarzenbach (Z. Elektrochem. 44, 46-55 (1938)). He makes assumptions in regard to the exchange reaction constants between the varieties of water and the varieties of oxonium ions, which are equivalent to the assumption that $K_4^{1/3}$ and $K_5^{1/3}$ are each equal to the simple statistical value 3. His value for the constant corresponding to K_6 is 1/7.72, owing to the different choice of the normal electrode potential of deuterium.

Acid-Base Equilibria in Aqueous and Non-aqueous Solutions (page 259).

L. J. MINNICK AND MARTIN KILPATRICK (University of Pennsylvania).

M. KILPATRICK (University of Pennsylvania): The following corrections should be made: In equation 4 on page 265 $D_0T^{3/2}$ should be $(D_0T)^{3/2}$. Equation 13 on page 273 should read

$$\cdots = \frac{\Delta WD}{2.30RT} = \frac{-V_{\bullet 1}D}{2.30RT}$$

In conformity with equations 9 and 10, L is proportional to $1/T$, and equation 14 becomes

$$V_{\bullet 1} = \frac{-2.303LRT}{D} = \frac{A}{D} \quad (14)$$

where $A \neq f(T)$

$$\Delta S = \frac{-d\Delta F}{dT} = \frac{A}{D^2} \frac{dD}{dT} = V_{\bullet 1} \frac{d \ln D}{dT} \quad (15)$$

and for water as solvent

$$\Delta S = -0.005 V_{\bullet 1} \quad (16)$$

The values of the electrostatic entropy in the last column of table 10 (page 272) should be reduced to five-eighths of the values given. These entropies correspond with those calculated from ΔF and ΔH (8) in sign and in order of magnitude for the substituted benzoic acids, but, as pointed out by Hammett, they differ widely in the case of the aliphatic acids.

J. G. KIRKWOOD (Cornell University): Gurney's criterion for estimating the relative importance of electrostatic and exchange forces in the free energy of transfer of a proton from an acid to a base is open to certain objections. Recent calculations of Westheimer and myself show that the electrostatic part of the free energy is not proportional to the reciprocal of the solvent dielectric constant, as Gurney assumes, but is a rather complicated function of this quantity. In many cases the electrostatic free energy of transfer is quite insensitive to the solvent dielectric constant and would be classified as non-electrostatic by Gurney's criterion. It cannot be denied that exchange forces play an important rôle in the dissociation of weak acids. However, owing to their short range character, it is reasonable to suppose that they are very nearly the same in molecules carrying acidic groups of the same structure, as, for example, the aliphatic carboxylic acids. They would then cancel in the calculation of the relative dissociation constant of two such acids.

Experimental Studies of the Ionization of Acetic Acid (page 275). HERBERT S. HARNED (Yale University).

H. S. HARNED (Yale University): The symbols identifying the points

are omitted from the legend of figure 1 on page 279. They are, reading from top to bottom of the legend in order: \odot , \boxplus , \boxminus , and $-\boxminus$.

SUMMARY

J. H. HILDEBRAND (University of California): I am tempted, as we close, to speak of certain contrasts between the language and points of view characteristic of our first day's program and those of today. The investigators of electrolytic solutions are at home only at infinite dilution, where, however, they cannot make any measurements. Now it is a long, long way to infinite dilution, and the usual processes suffer from difficulties comparable to those that would attend finding one's way between two villages in Flanders by going *via* Tipperary. I believe it would be worth while to try, for a change, some other standard state nearer at hand, such as the pure solid. This would make it possible to go from one solvent to another without getting lost. It is easy to forget that activity coefficients at infinite dilution in different solvents have nothing whatever in common.

Another difference lies in the treatment of the solvent by workers with non-electrolytic solutions as a molecular species worthy of the same dignity as the solute, but by workers with electrolytic solutions simply as space with a dielectric constant. I think the latter will eventually have to adopt some of the language of the former. Water is a chemical substance. The actual geometry of polar molecules must be taken into account in addition to dipole moment.

Finally, in all but extremely dilute solutions, mole fraction, as advised some time ago by Dr. Scatchard, will, I predict, replace volume concentration and molality. The results that I have presented for the simple case of paraffin solutions emphasize the importance of the size of the solvent molecules. This may be masked by other factors in the more complex solutions, but it does not disappear. I predict that in our next symposium on solutions our points of view will be found convergent.

G. SCATCHARD (Massachusetts Institute of Technology): As I review what has crystallized as written discussion from the fluid verbal remarks at the Symposium, it seems desirable to add a few words which I would have felt superfluous at the Symposium itself. I have worked more or less in every field covered by this Symposium, and I can assure Professor Hildebrand that nothing which I know when I work with non-polar mixtures is forgotten when I work with ions or dipolar ions. Furthermore, I truly believe that a larger fraction of the workers in the latter fields than in the former keep in mind the points that he has raised.

There are times when we do follow Professor Hildebrand's suggestion to avoid infinite dilution, but more often it is not desirable to do so if we are looking for a theoretical interpretation. It was hardly worth while to

leave one village in Flanders just to go to another village in Flanders; it was going to Tipperary that mattered.

The other differences Professor Hildebrand finds are, I believe, largely matters of language. For example, the volume fractions which he and I use to measure compositions of non-polar mixtures may be regarded as concentrations in such units that the concentration of each pure liquid is unity. Also, although we do not forget the molecular structure of the solvent, there is little use in talking about it until a model recognizing this structure yields more accurate calculations than the crude model which ignores it.

Like Professor Hildebrand, I felt that there was a difference between the first day and the last, but my interpretation of this difference is not the same as his. Since this Symposium coincided with the dedication of the new Metcalf Research Laboratory, it seems natural to compare the Symposium to a building. The first day we spent in a new wing, where the tenants were explaining the façade and the floor plan as a whole, even where the building was still only scaffolding. The last day we were in a wing which had been occupied for fifteen years by the same tenants and had had no large scale alterations for several years, so that the talk was largely of the perfecting of relatively small bits of hardware or furniture with a tacit assumption that everyone knew the general architectural plan.

The fact that our ideas are less far apart than the words we use to tell of them can perhaps be expressed best by the speech of Senator Metcalf as he presented the keys to President Wriston a second time for the benefit of the news photographer who missed the first presentation,—“Same keys, same building, just another picture.”

THE ENTROPY OF SOLUTION OF HEXANE WITH HEXADECANE

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Received December 21, 1938

In a section of the contribution¹ by the senior author to the Symposium on Intermolecular Action some experimental figures were presented indicating that normal hexane and normal hexadecane form ideal solutions in accordance with an earlier prediction. At the same time mention was made of further experimental verifications then under way. This work has now been completed and is reported here.

Since hexane and hexadecane must be synthesized in order to guarantee adequate purity and are rather expensive, it was desirable to use a method requiring but small quantities. We had small samples of these hydrocarbons, which had been obtained from the Eastman Kodak Company.

The vapor pressure of hexadecane is so minute at room temperatures that it is unnecessary to determine the composition of the vapor phase over the solution, the vapor pressure being due solely to hexane. Measurements were carried out in the tensimeter illustrated in figure 1. The calibrated tube, A, contains pure hexane. The amount present in the tube at any one time is determined by a cathetometer reading of the distance of the meniscus above the mark etched in the glass while the tube A is immersed in a bath of known temperature. The bulb, B, contains a known amount of hexadecane introduced from a weight pipet prior to sealing. Both components are frozen by the aid of liquid air, the mercury serving as a manometer is poured into the bulb, C, and the apparatus is evacuated through the stopcock. The mercury is then poured down into the triple manometer stems, and both substances are melted. A small amount of air is of course present in both hydrocarbons, but it is largely expelled on freezing and escapes as small bubbles during the subsequent melting. This freezing and melting is repeated several times, after which the hydrocarbons are finally frozen and the apparatus re-evacuated. A certain amount of hexane is then distilled from A into B, giving a solution whose composition is determined by freezing both components, pouring the mercury into the manometer, melting the hexane,

¹ J. Phys. Chem. **43**, 109 (1939).

and determining the new height of its meniscus. Portions A and B of the apparatus are then placed in a large thermostat, the manometer portion being outside in a glass-enclosed box maintained at somewhat higher temperature in order to prevent distillation of the hexane onto the mercury. Readings of the three mercury columns permit the simultaneous determination of the vapor pressures of hexane over the solution and over the pure liquid. Since these two pressures will normally have about the same temperature coefficients in the case of regular solutions and, in the present system exactly the same coefficient, extreme accuracy in temperature control is unnecessary. Equilibrium is attained so quickly that the

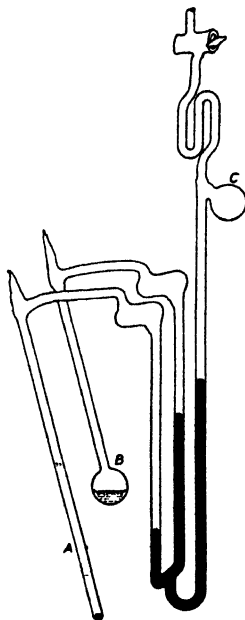


FIG. 1. The tensimeter

well-insulated thermostat remains constant in temperature within 0.002°C . over periods of time far in excess of the period of a single measurement. A number of different compositions can be investigated with a single filling of the apparatus simply by repeating the distillation in either direction as desired.

The results are given in table 1 and plotted in figure 2. Series 1 represents the results previously reported, obtained by another method. It will be seen, first, that the ratio of the vapor pressure of hexane from the solution to that from the pure liquid, p/p^0 , agrees with its mole fraction, N , within what is doubtless the experimental error. This agreement is closest for the second series of measurements, where the manipulation

TABLE 1

SERIES	TEMPERATURE	p	p^0	$\frac{p}{p^0}$	MOLE FRACTION HEXANE N	$\frac{p}{p^0 N}$
	°C.	mm.	mm.			
1	25.0	106.2	149.7	0.708	0.708	1.000
	25.0	99.6	149.7	0.665	0.648	1.025
	25.0	92.7	149.7	0.619	0.626	0.989
2	25.00	111.3	150.4	0.740	0.738	1.002
	25.00	111.7	150.7	0.742	0.738	1.004
	25.00	111.7	150.7	0.742	0.738	1.004
	25.00	66.8	150.9	0.443	0.430	1.029
	25.00	66.9	150.9	0.443	0.430	1.029
3	25.01	102.5	155.3	0.660	0.663	0.996
	25.01	102.6	154.9	0.662	0.663	0.998
	25.01	102.5	154.7	0.663	0.663	1.000
	25.01	102.8	154.7	0.664	0.663	1.002
	25.00	96.5	153.0	0.631	0.635	0.994
	25.00	96.5	153.0	0.631	0.635	0.994
	24.8	72.9	153.3	0.476	0.478	0.996
	25.02	74.3	155.6	0.478	0.478	1.000
	25.01	73.7	155.8	0.473	0.478	0.989
	25.01	73.6	155.8	0.473	0.478	0.989
	14.0	44.7	91.6	0.489	0.478	1.023
	17.8	24.0	110.4	0.217	0.222	0.978
	19.8	27.7	123.9	0.223	0.222	1.003
	20.0	28.0	125.2	0.224	0.222	1.008
	23.2	31.9	143.0	0.223	0.222	1.003
	23.4	31.9	144.2	0.221	0.222	0.996
	25.00	33.3	154.7	0.215	0.222	0.969
	25.00	33.6	156.0	0.215	0.222	0.969
	25.00	33.7	157.0	0.215	0.222	0.969

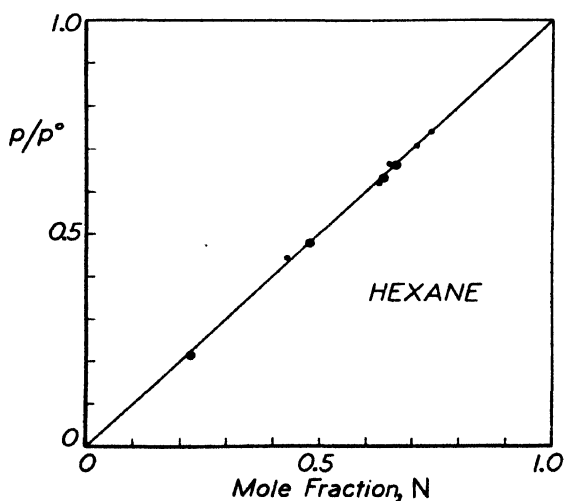


Fig. 2. Relative vapor pressures of hexane from solutions with hexadecane

was carried out with the greatest care. The small discrepancies between the values of p^0 at 25.00°C. may be attributed mainly to the use of different samples of hexane and should have but little effect upon the ratio, p/p^0 . It will be seen, also, that the ratio p/p^0 is practically independent of temperature, a further and most direct evidence that the entropy of solution follows Raoult's law. This system, therefore, corresponds excellently with the model used in analyzing the possible configurations in a system of linear molecules of different lengths in parallel arrangement.

HYDROPHIL BALANCE STUDIES ON HIGH MOLECULAR WEIGHT KETONES

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INTRODUCTION

The correlation between the film characteristics of several related ketones and the type of organic radical attached to the respective carbonyl groups has been studied by means of hydrophil balance measurements. For this purpose we chose a series of ketones containing one straight-chain aliphatic R group of seventeen members with the other R group varying throughout the series. The compounds selected as representative of such a series were as follows: methyl heptadecyl ketone, stearone, biphenyl heptadecyl ketone, and phenoxyphenyl heptadecyl ketone. Stearic acid was also included in the study for the purpose of making comparisons with published data (1).

Methyl heptadecyl ketone and stearone were selected because the former contains the smallest possible aliphatic group, whereas the latter contains a relatively long aliphatic group. On the other hand, biphenyl heptadecyl ketone and phenoxyphenyl heptadecyl ketone contain aryl groups which are similar except for the presence of an ether oxygen linkage between the two phenyl groups in the case of the latter ketone. The rôle of this ether oxygen in the molecule was thought to be of particular interest because of its possible hydrophilic nature.

Formulas, molecular weights, and observed melting points are listed in table 1.

EXPERIMENTAL PROCEDURE

Preparation of materials

Methyl heptadecyl ketone was prepared from stearonitrile and methylmagnesium iodide by means of the Grignard reaction. The product was recrystallized until the melting point was constant.

Stearone was prepared by passing stearic acid, at a rate of about 30 g.

per hour, over manganese chromite catalyst in an electric furnace heated at $410^{\circ}\text{C.} \pm 10^{\circ}$. The product was recrystallized from a mixture of ethanol and benzene until a constant melting point was obtained.

Biphenyl heptadecyl ketone was prepared by means of the Friedel-Crafts reaction from biphenyl and stearoyl chloride (5). The product was recrystallized from acetone until the melting point was constant.

Phenoxyphenyl heptadecyl ketone was prepared by means of the Friedel-Crafts reaction from phenyl ether and stearoyl chloride (5). The product was recrystallized from acetone until crystals of constant melting point were obtained.

The benzene used in preparing the solutions was Baker's thiophene-free benzene. Prior to use, it was fractionated twice through an eight-ball air-jacketed Snyder distilling column made entirely of glass. All joints were ground glass, and no stopcocks were used in the apparatus.

TABLE 1

Formulas, molecular weights, and melting points of stearic acid and the ketones

COMPOUND	FORMULA	MOLECULAR WEIGHT	MELTING POINT °C.
Stearic acid	$\text{C}_{17}\text{H}_{35}\text{COOH}$	284.3	70.0-0.5
Methyl heptadecyl ketone	$\text{C}_{17}\text{H}_{35}\text{COCH}_3$	282.3	55-6
Stearone	$\text{C}_{17}\text{H}_{35}\text{COC}_{17}\text{H}_{35}$	506.5	86-7
Biphenyl heptadecyl ketone	$\text{C}_{17}\text{H}_{35}\text{CO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$	420.3	104-6
Phenoxyphenyl heptadecyl ketone	$\text{C}_{17}\text{H}_{35}\text{CO}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_5$	436.3	63-5

Apparatus

The hydrophil balance used in this study was of a modified Langmuir-Adam type (4). The tray used was an aluminum casting approximately 14 x 65 cm. with a phosphor bronze float attached to the sides of the tray by means of gold ribbons 4 mm. wide and 0.012 mm. thick. The force on the float was measured by means of a steel torsion wire 0.21 mm. in diameter. The sensitivity necessary for precision measurements was attained by the use of a mirror and a beam of light reflected to a screen at a distance of 100 cm. It was necessary to cover the aluminum tray with a thick layer of parowax. No hydrogen bubbles were observed with the 0.01 *N* hydrochloric acid solutions which were used throughout the investigation.

The movable barriers used were of brass, coated with a thin film of parowax. The barriers were moved continuously for all observations by means of a rack and pinion driven by a one revolution per minute synchronous motor. Four constant speeds were available: namely, 60, 20, 6.6, and

2.2 mm. per minute. This was an important item in the experimental setup as used in this investigation, because film balance force-area measurements are dependent in their absolute values upon the rate of compression of the film. In this first study on the series most of the data were obtained at the 20 mm. per minute speed. In future work the effect of changes in rate of compression will be studied.

Observations were made by setting the torsion head wire at successive steps of rotation. The barrier position was read on the scale at the moment the beam of light reflected from the torsion wire mirror reached the zero or equilibrium point on its scale. The zero point shifted with slight changes in the level of the water in the tray; hence this fact was advantageously used as a means of measurement in keeping the water level constant. No inconsistencies arose in the data obtained for the series of compounds under investigation if the water was used more than once, provided care was taken to maintain a constant water level.

Although rate of compression and water level are important factors in force-area measurements, changes in temperature are even more important because of their marked effect on film characteristics. Constant temperatures were attained by housing the film balance in a case consisting of a hair-felt-insulated, double-walled, copper box so arranged with channels between the double walls that water from a circulating thermostat could be circulated through five sides of the box. The front of the box had double glass doors, and, except for the small openings through which observations were made, the doors were covered with aluminum foil to reduce radiation. No difficulty was encountered in maintaining the temperature of the box at $25.0^{\circ}\text{C.} \pm 0.1^{\circ}$. This, however, was not true for the water in the tray itself, because of the cooling due to evaporation from the surface. This effect was especially important during the winter days of relatively low humidity. To obtain consistency in surface temperature it was necessary to install trays of water with an extensive system of wicks. This arrangement aided surface temperature control, but it was not adequate until portholes fitted with rubber sleeves were installed in the front glass so that a sample could be delivered to the surface of the water without admitting any appreciable quantity of dry air. The water in the film balance tray could also be changed without opening the case. In its final form, the case permitted the surface temperature of the tray to be held constant within 0.1°C.

Samples dissolved in carefully distilled benzene were used throughout the investigation, although check runs were made with petroleum ether whenever solubility permitted. Samples were measured by the use of an automatic microvolume pipet (3). The pipet was calibrated volumetrically, in an atmosphere saturated with benzene, for each sample. It was necessary to calibrate the pipet with each solution because with a pipet as

TABLE 2
Quantities and concentrations of solutions used









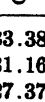
COMPOUND	VOLUME OF SAMPLE	CONCENTRATION
	cc.	grams per cc.
$C_{17}H_{35}COOH$	0.0428	0.00153
$C_{17}H_{35}COCH_3$	0.0427	0.00202
$C_{17}H_{35}COC_{17}H_{35}$	0.0854	0.00131
$C_{17}H_{35}CO$ -  - 	0.0435	0.00315
$C_{17}H_{35}CO$ -  -O- 	0.0426	0.00330

TABLE 3
Data obtained in force-area measurements

FORCE IN DYNES PER CENTIMETER	AREA PER MOLECULE IN Å ²				
	$C_{17}H_{35}COOH$	$C_{17}H_{35}COCH_3$	$C_{17}H_{35}COC_{17}H_{35}$	 $C_{17}H_{35}CO$ - 	 O-  $C_{17}H_{35}CO$ - 
0.26	28.05	21.53	43.62	25.14	33.38
0.52	26.24	21.36	39.28	22.36	31.16
1.29	25.89	21.15	34.88	18.68	27.37
2.59	25.54	20.91	31.91	17.31	24.75
3.88				16.43	23.39
5.18	24.88	20.49	28.34	15.81	22.35
7.76	24.26	20.40	26.01	14.84	20.94
10.35	23.72	20.33	24.12	14.13	19.99
12.94	23.15	20.28	22.58	13.53	19.16
15.53	22.59	20.21	21.08	13.04	18.44
18.12	22.09	20.16	19.85	12.58	17.64
20.70	21.66	20.11	18.78	12.15	16.91
23.29	21.18	20.05	17.69	11.77	16.05
25.88	20.80	20.00	16.57	11.40	14.97
28.47		19.95	15.63	10.99	13.78
31.06		19.89	14.86	10.63	12.77
33.64		19.84	14.12	10.30	12.14
36.23	20.43	19.79	13.56	9.97	11.68
38.82		19.71	13.04	9.61	11.24
41.41		19.68	12.51	9.35	10.88
44.00		19.63	12.06	9.09	10.58
46.58	20.04		11.63	8.85	10.27
51.76			10.73	8.29	9.61
56.94			10.00	7.76	9.02
62.11			8.99		
64.70			8.46		

small as the one used, 0.043 cc., the area was large compared to the volume. This resulted in an appreciable quantity of solution remaining on the walls of the pipet. It may be of interest in the future when more data are available to work out a correlation between the film characteristics and the delivery volume. It was necessary to deliver only a very small sample of the solution to the tray to avoid dissolving parowax from the sides of the relatively narrow tray.

The quantities and concentrations of the solutions used are given in table 2.

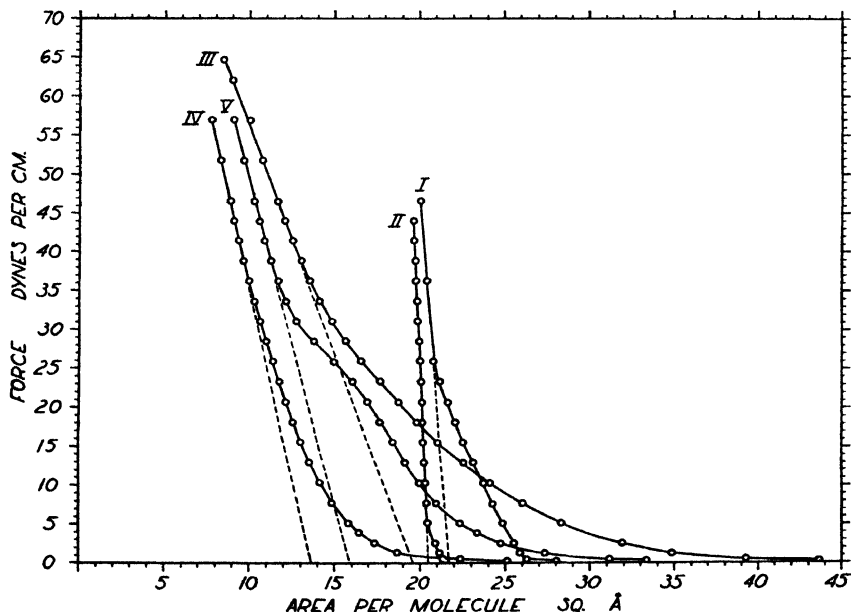


FIG. 1. Force-area measurements on films of stearic acid (I), methyl heptadecyl ketone (II), stearone (III), biphenyl heptadecyl ketone (IV), and phenoxyphenyl heptadecyl ketone (V).

The film balance equipment was constructed so that in the future films might be studied through a range of temperatures and at different rates of compression. Studies at different hydrogen-ion concentrations may also be made. The use of a wider tray of a material other than aluminum is contemplated for these additional measurements.

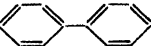
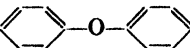
RESULTS

Force-area measurements were made on each of the films under exactly similar experimental conditions. The data obtained were averaged and are presented in table 3 and figure 1. It was found that individual readings did not differ from the average value by more than 4 per cent.

The extrapolated values of the molecular areas were read from figure 1, where they are indicated for the upper portion of the curves by the broken lines. The broken lines for the lower portion of the curves are omitted to avoid confusion on the graph. These values are listed in table 4. Since methyl heptadecyl ketone, stearone, and biphenyl heptadecyl ketone do not have any lower slopes, no extrapolated values are listed.

The nature of the films was also studied by means of lycopodium powder and a stream of air. It was found that methyl heptadecyl ketone was free moving at all compressions. Stearone had about the same rigidity as stearic acid. Biphenyl heptadecyl ketone and phenoxyphenyl heptadecyl ketone are very much more rigid than stearic acid.

TABLE 4
Extrapolated values of the molecular areas

COMPOUND	AREA PER MOLECULE IN Å ²	
	Upper portion	Lower portion
C ₁₇ H ₃₅ COOH	21.7	26.1
C ₁₇ H ₃₅ COCH ₃	20.5	
C ₁₇ H ₃₅ COC ₁₇ H ₃₅	19.7	
C ₁₇ H ₃₅ CO- 	13.7	
C ₁₇ H ₃₅ CO- 	15.9	22.9

CONCLUSIONS

From the force-area curves of figure 1 it is evident that the film of stearone is more compressible than that of methyl heptadecyl ketone. This fact, together with our observation that methyl heptadecyl ketone is a free moving film even at the highest compression, leads us to believe that there is a high repulsion between the molecules of methyl heptadecyl ketone. We interpret this as due to the non-symmetrical nature of methyl heptadecyl ketone as compared to stearone.

From the curves in figure 1 it is evident that at low pressures (expanded film) the area of the phenoxyphenyl heptadecyl ketone molecule is considerably greater than that of the biphenyl heptadecyl ketone molecule, while at high pressures the two curves approach each other quite closely. This observation can be explained by attributing hydrophilic properties to the ether oxygen in the phenoxyphenyl heptadecyl ketone molecule. As the force on the film is increased the ether oxygen is removed from contact with the water (as the force increases from 21 to 36 dynes per centimeter), and the two areas become approximately the same. The ether oxygen should exhibit hydrophilic character because of its four unshared electrons, but this effect should be considerably less than that of the carbonyl oxygen

because of the steric effect of the adjacent phenyl groups. Experimental results appear to conform to this prediction.

Comparisons between various hydrophil balance studies are unreliable because of the influence of numerous factors involved in the experimental technique: *viz.*, rate of compression of the film, time elapsing between the application of the film and the start of the run, the amount of contamination, the age and the pH of the aqueous solution in the tray, and the temperature. From our own observations we conclude that the relative humidity of the surrounding atmosphere plays an important rôle in temperature control.

Since biphenyl heptadecyl ketone and phenoxyphenyl heptadecyl ketone are relatively new compounds, no film balance data are available for comparison. Our force-area curve for methyl heptadecyl ketone is in excellent agreement with that obtained by Adam, Danielli, and Harding (2). These same authors state that in an attempt to spread stearone a scarcely perceptible surface pressure was observed. This result does not agree with our observations.

Various values for the molecular area of stearic acid have been reported. Harkins and Anderson (3) report a value of 23.8 \AA^2 for the expanded film and 20.4 \AA^2 for the condensed film at zero pressure. Adam (1) reports a value of 24.9 \AA^2 for the expanded film and 21.0 \AA^2 for the condensed film. These are at some variance with our values of 26.1 and 21.7 \AA^2 for the expanded and condensed films, respectively.

Further work, in which the effect of temperature, pH, and the rate of compression of the films of these and related compounds will be studied, is contemplated. It is hoped that these further data will permit more extensive conclusions regarding the behavior of these compounds.

SUMMARY

1. Hydrophil balance studies have been made on a series of several related ketones: *viz.*, methyl heptadecyl ketone, stearone, biphenyl heptadecyl ketone, and phenoxyphenyl heptadecyl ketone.

2. Important refinements in the usual apparatus for film studies permitting careful temperature and humidity control have been outlined.

3. An explanation has been offered for the behavior of these films under compression.

REFERENCES

- (1) ADAM, N. K.: *The Physics and Chemistry of Surfaces*, p. 47. Clarendon Press, Oxford (1930).
- (2) ADAM, N. K., DANIELLI, J. F., AND HARDING, J. B.: *Proc. Roy. Soc. (London)* **A147**, 491-9 (1934).
- (3) HARKINS, W. D., AND ANDERSON, T. F.: *J. Am. Chem. Soc.* **59**, 2189-97 (1937).
- (4) HARKINS, W. D., AND MYERS, R. J.: *J. Chem. Phys.* **4**, 716 (1936).
- (5) RALSTON, A. W., AND CHRISTENSEN, C. W.: *Ind. Eng. Chem.* **29**, 194-6 (1937).

ADSORPTION OF WATER BY PAPERS AT ELEVATED TEMPERATURES

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INTRODUCTION

While a large quantity of data is available on the adsorption characteristics of water on various forms of cellulose, for the most part the important region of low equilibrium water vapor pressure and high temperature has been neglected. Urquhart and Williams (13) have compiled much data on the adsorption of water on cotton over the complete humidity range and at temperatures up to 110°C. Others (6, 9, 10) have covered similar conditions for other cellulosic materials. In the region first mentioned information regarding the quantity of water adsorbed on cellulosic materials is essential, as papers are frequently impregnated with waxes or oils at from 100° to 150°C., under reduced pressures, for use as electrical insulation. Slight variation in the small quantities of water remaining influences greatly the insulation resistance and other properties of cellulosic materials (3). Accordingly, the equilibria have been extensively investigated between water and two types of paper, one processed from linen rag and the other from kraft wood pulp. Both papers are super-calendered condenser tissue less than 0.5 mil in thickness. The temperature of test varied from 100°C. to 150°C., and equilibrium relative vapor pressures from 0 to 3 per cent were obtained. Data in this temperature and pressure range should also aid in advancing the knowledge of the mechanism of water adsorption on cellulose and of the structure of cellulose itself.

EXPERIMENTAL

The sorption was measured by the addition of accurately measured quantities of water to the sample of known dry weight, subtracting the quantity of water existing as vapor in equilibrium with the sample from the quantity admitted to determine the amount adsorbed. For the present purpose this procedure is more accurate than the method of direct weighing, which cannot be used here because of the small quantities of water sorbed.

The apparatus employed is shown schematically in figure 1, and is constructed entirely of glass. Bulb A, the volume of which between the stop-

cocks was calibrated with water, is used to determine the volume of the whole and of separate sections of the completed apparatus. B is a mercury manometer, read with a cathetometer accurate to ± 0.02 mm. of mercury. Corrections are applied to the manometer readings to remove the error caused by unequal meniscus heights. This is a small correction, seldom being greater than the error incurred in reading the manometer. C is a bulb of about 500-cc. volume, independently calibrated. It is employed in desorption measurements and has a short capillary tube attached to facilitate freezing-out operations. D is a small bulb set on a capillary tube, in which the water from the system may be collected by freezing out with dry ice and acetone. G_1 , G_2 , and G_3 are capillary tubes 85 cm. long

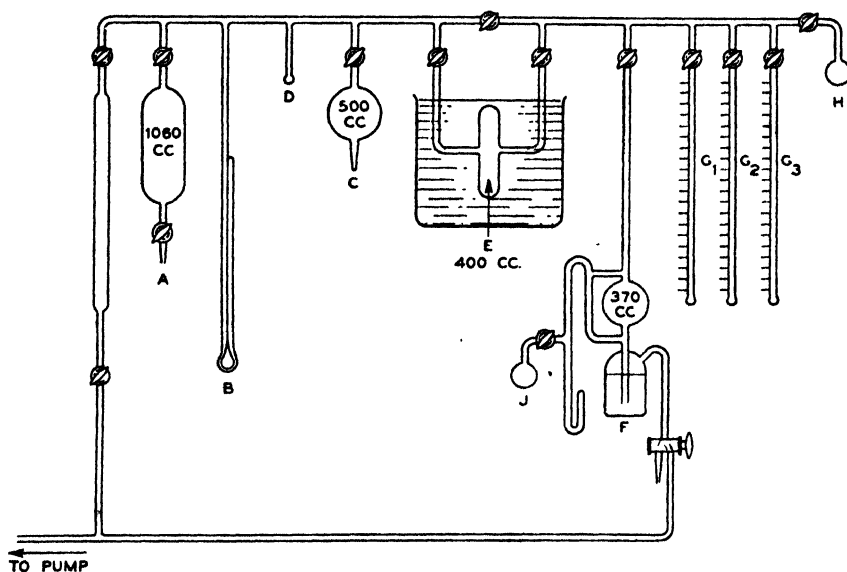


FIG. 1. Schematic diagram of adsorption apparatus

and averaging 1.34 mm. in diameter, accurately calibrated with a mercury thread. Water for the sorption experiments is distilled into the capillaries from the small bulb H, where it has been thoroughly degassed by alternate freezing and melting under vacuum. Distillation from the bulb to the tubes is effected by a slight temperature difference, as too rapid distillation causes gaps to form in the water columns. Although in reading the water level in the capillary a small mirror is the only aid, the error of reading is only ± 0.0002 g. of water, an error which will be the same regardless of the total quantity of water evaporated from the tube, for the original water level in the capillary is held as reference throughout a series of measurements. This method, then, for measuring admitted water incurs a rather

large error for a single admission, possibly 2 per cent, but with additional admissions the percentage error decreases to a negligible value at completion of a series of measurements.

The method outlined above for measurement of water was used in obtaining a part of the data reported. However, certain difficulties of manipulation made it advisable to employ a second method, which for most purposes offers greater ease of operation. This is particularly true when the quantities of water measured are comparatively small, as in the work at the higher temperatures. This second method makes use of the calibrated bulb and mercury well F. Water is admitted as vapor to the large bulb from the small bulb J, containing liquid water, purified as in the case of bulb H. The pressure of the water vapor in the bulb is read with the aid of a small mirror on the attached manometer. The water vapor is then displaced into the system by flushing out the bulb with mercury. This procedure incurs probably about the same error for a single measurement as the capillary method, but has the disadvantage that the error may be to some extent cumulative. Increased ease of operation, however, is a not inconsiderable factor in choosing between the two procedures.

E is the tube containing the sample, and is immersed in a bath which is maintained at constant temperature. Thermocouple measurements indicate that a regulation of $\pm 0.05^{\circ}\text{C}$. is obtained.

The samples are taken from rolls of tissue and wound loosely into cylinders. They are weighed in the dry condition after being heated at 100°C . under vacuum for at least 8 hr. This treatment is considered to give an essentially dry paper, although the treatment is necessarily arbitrary (1), for it appears in the light of the results obtained that in a theoretical sense the paper cannot be obtained in the dry state without disintegration occurring under the extreme conditions necessary to complete drying. The same treatment is given the sample at the beginning of each series of measurements.

Correction was made in all measurements for the thermal decomposition of the paper. This is a small correction at 100°C ., but becomes of increasing importance with increasing temperature. In one system employed, for example, the permanent gas pressure (gases other than water vapor) increased 0.07 mm. per hour, while 0.04 mg. of water was formed per hour at 150°C .

RESULTS

The two types of paper were examined over a similar range of conditions. Initial measurements were made at 100°C ., the relative vapor pressure varying from zero to the maximum obtainable, which was limited by the external temperature and was approximately 3.5 per cent. Additional series of measurements were made at 110°C ., 120°C ., 130°C ., and 150°C .

The relative vapor pressure range decreased with increasing temperature, with a maximum of 0.7 per cent available at 150°C. Graphical representation of the adsorption isotherms is shown in figure 2 for the linen rag paper, and in figure 3 for the wood pulp paper. The two sets of curves are alike in type, but the paper derived from wood pulp exhibits a considerably higher adsorption under all conditions.

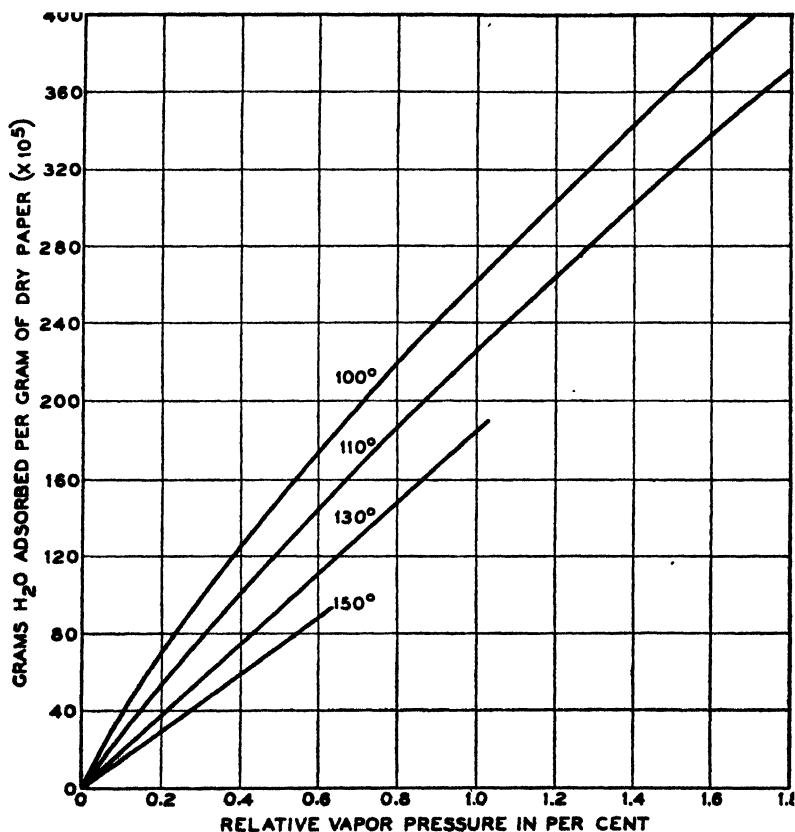


Fig. 2. Adsorption of water by linen rag paper

It will be noticed that the 120°C. isotherm for the linen rag paper is missing, while the 110°C. isotherm for wood pulp paper does not appear to fit into the other curves of that family. The reason for the omission of the one and the error of the other is due to the fact that, in preparation of the sample for those particular series of measurements, the samples were subjected to temperatures above those at which the measurements were made.

The isotherms obtained in this low relative vapor pressure range may be expressed accurately by means of the Freundlich adsorption equation,

which has been extensively employed by Freundlich and others to express mathematically the adsorption of vapors by porous solids, and which in general form is

$$\alpha = Ap^{1/n}$$

where α is the quantity of adsorbed material per unit quantity of adsorbent, p is the pressure of the vapor in equilibrium with the adsorbent, and A

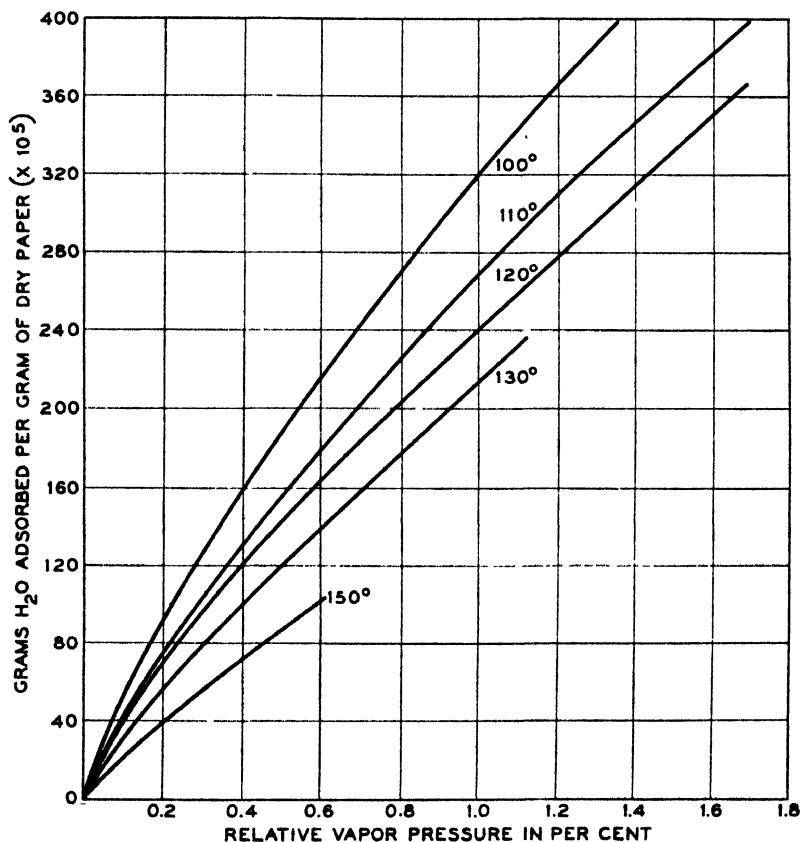


Fig. 3. Adsorption of water by kraft process wood pulp paper

and $1/n$ are constants. The accuracy with which the isotherms may be expressed in this form is shown by the graphs of figures 4 and 5.

Each isotherm, then, may be expressed by an equation of the Freundlich type, the equations differing only in the values of the constants. Table 1 lists the two constants $\log A$ and $1/n$ with respect to the temperature for the isotherms measured on the two papers. For neither paper does the value of the constant A appear to be approaching a limiting value with

increasing temperature. The constant $1/n$, however, approaches unity rapidly, reaching that value within 1 per cent below 150°C . in the case of the linen paper. For the wood pulp paper, the curve of $1/n$ against T is linear, in the region studied, as the curve of figure 6 indicates. Since $1/n$ is not expected to become larger than unity, it may be assumed to remain constant at all higher temperatures. Under this condition the isotherm itself is linear, and this has been observed to be the case in numerous vapor-adsorbent systems, notably for carbon dioxide adsorption on wood

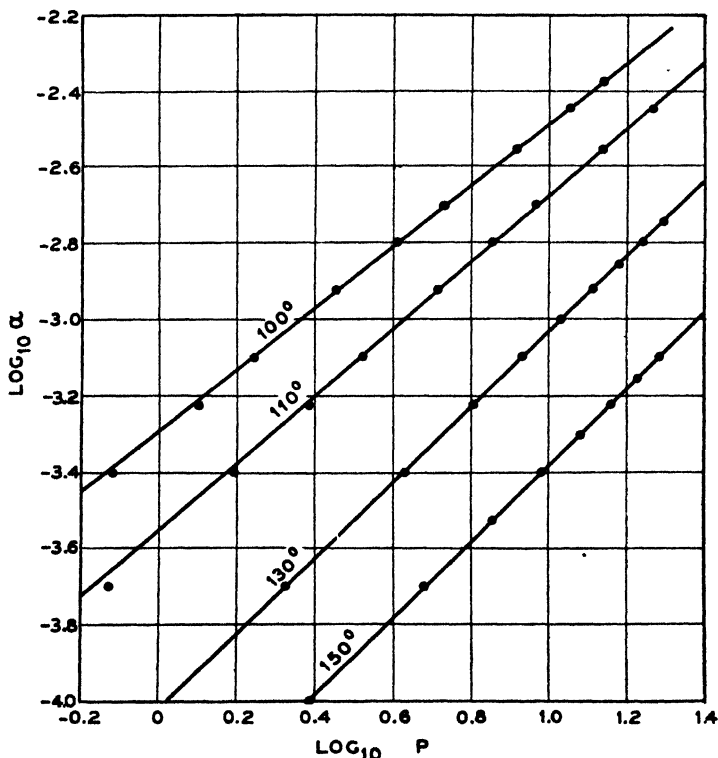


FIG. 4. Plot of curves of figure 2 on logarithmic scale

pulp, as determined by Salley (7). In the same paper Salley finds the isotherms for water adsorption on wood pulps to be linear at concentrations of adsorbed water of 0.00016 g. per gram and less.

All of the isotherms obtained are adsorption isotherms, and no desorption measurements were made other than several of a qualitative nature. The few measurements made, however, indicate a definite hysteresis existing between the quantity of water held on adsorption and that held on desorption. The hysteresis was on the order of 5 per cent at 100°C . and 1.6 per cent R.H. This value is probably somewhat smaller than the real

hysteresis, for, according to Pidgeon (5), attainment of equilibrium accompanied by changing vapor pressure, which occurs as a consequence of the

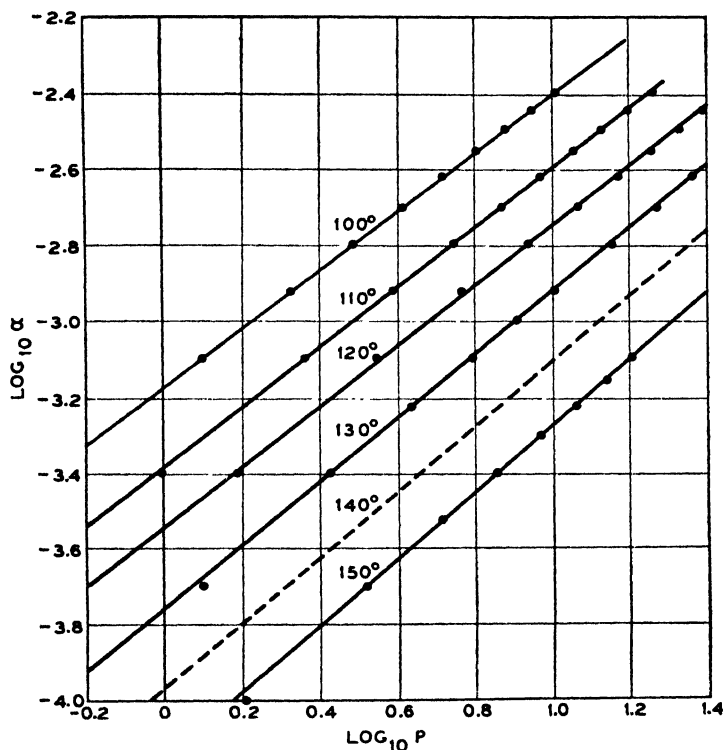


FIG. 5. Plot of curves of figure 3 on logarithmic scale

TABLE 1
Values of $\log A$ and $1/n$

PAPER	T	$\log A$	$1/n$
Linen.....	100	-3.292	0.802
	110	-3.552	0.872
	130	-4.021	0.989
	150	-4.375	0.991
Kraft.....	100	-3.173	0.767
	110	-3.383	0.783
	120	-3.540	0.796
	130	-3.757	0.837
	150	-4.150	0.879

procedure employed in this instance, tends to decrease the area of the hysteresis loop. However, the rapid attainment of equilibrium at 100°C.

and the large number of admissions of water required to obtain the isotherm, which is but 3 per cent of the entire length of the isotherm, minimize the error incurred, and the difference from the true hysteresis is probably small. In any event, the data indicate that hysteresis continues

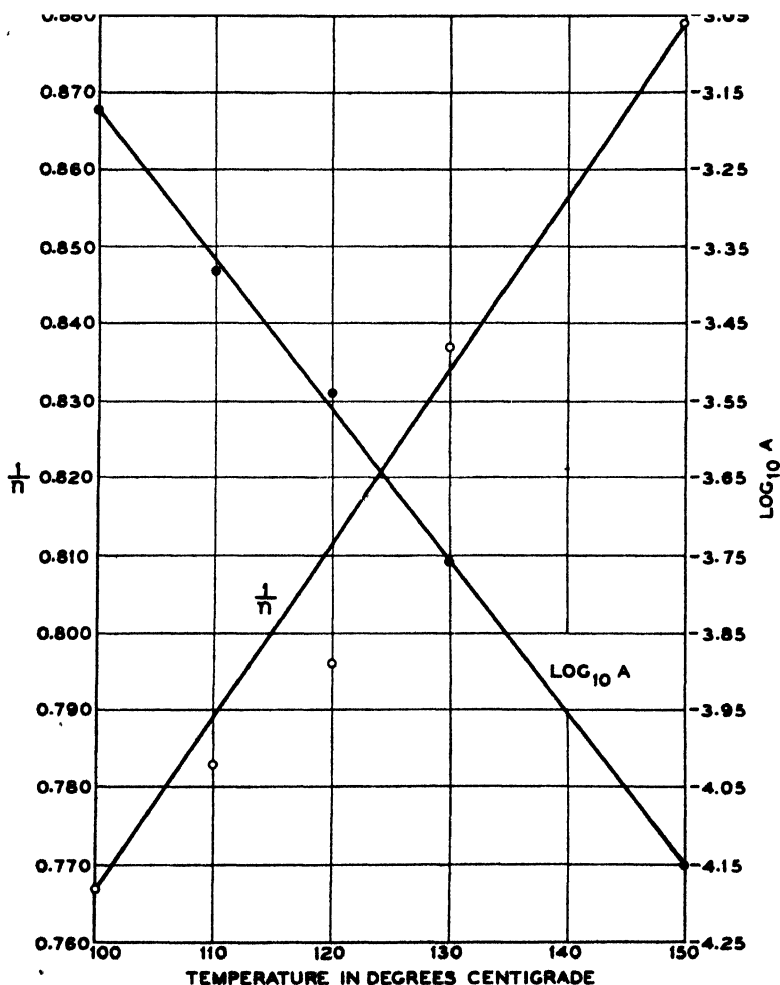


FIG. 6. Plot of constants from table for kraft process wood pulp paper

well into the region of slight adsorption and may be present at all moisture contents.

The greater adsorption observed on the kraft wood pulp paper may be due in whole or in part to any one of a number of differences in the structure and composition of the two papers. Sufficient data are lacking, however, to attempt at present to assign the difference in adsorption to any

particular difference or differences in the papers. It is known, for instance, that the linen rag paper contains a much higher percentage of α -cellulose than does the wood pulp paper, but the differences among α -, β -, and γ -cellulose are not well defined. However, the observed reproducibility of the isotherms eliminates the possibility of chemical reaction in the ordinary sense with either the cellulose of the paper or the impurities contained in the paper. Also, adsorption by lignin, which is present in greater quan-

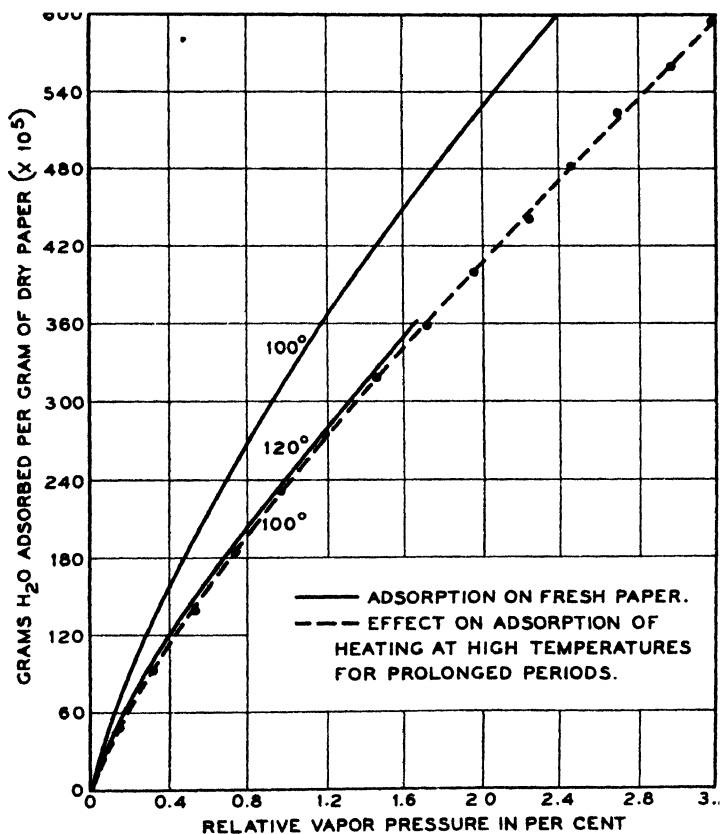


FIG. 7. Decrease in adsorption upon preheating kraft process wood pulp paper

tity in the wood pulp paper, cannot be the cause of the greater adsorption by the wood pulp paper, unless the process of lignin removal alters greatly its capacity for adsorption, for Seborg (8) has shown that cuprammonium lignin has essentially the same adsorption as the wood from which it is obtained. Other variables in the paper composition cannot, however, as yet be eliminated or confirmed as to their quantitative effect on moisture adsorption.

Mention was made previously of one isotherm being in error because the paper was dried at a temperature above that at which the isotherm was obtained. That the temperature of drying, or "preheating," has a large effect on the moisture adsorption is shown graphically in figure 7, where the isotherms for fresh paper at 100°C. and 120°C. are contrasted with the isotherm obtained at 100°C. on paper dried at about 170°C. While the curves shown are for the kraft wood pulp paper, the linen rag paper shows an almost identical decrease in adsorption. The per cent decrease is greater for the linen rag paper, however, since its adsorption in the fresh condition is smaller. This effect appears to be due to the temperature at which the adsorbent is dried, rather than the length of drying time. This conclusion is based on a series of qualitative measurements which showed the adsorption to be little affected by a reasonable increase in drying time. Data of a very similar nature have been obtained by Speakman and Stott (11) for the adsorption of water on wool and by Urquhart (12) for the adsorption of water on cotton.

Heats of adsorption have been calculated from the data obtained by employing an equation derived by Freundlich (2). It is of the form

$$\Delta H = \frac{-RT^2}{(1/n)} \left(-\frac{d \log A}{dT} - \log p \frac{d(1/n)}{dT} \right)$$

This equation can be altered to allow expression of ΔH in terms of α and T , making possible direct use of the isotherms and the log-log plots of the isotherms. This is done by substituting from the Freundlich adsorption equation

$$\log p = \frac{\log \alpha - \log A}{(1/n)}$$

into the heat of adsorption equation to give

$$\Delta H = \frac{-RT^2}{(1/n)} \left(\frac{d \log A}{dT} + \frac{(\log \alpha - \log A)}{(1/n)} \frac{d(1/n)}{dT} \right)$$

Values for $1/n$ and $\log A$, as tabulated, were obtained from the log-log plots of the isotherms. Values for the derivatives came from plots of these constants against temperature.

Assumptions must necessarily be made in the derivation of this equation, which to some extent invalidate the results obtained. The principal unwarranted assumption is that the structure of the adsorbent does not undergo alteration as the equilibrium temperature is increased. As shown by the curves illustrating the effect of preheating, the adsorption decreases with increased drying temperatures, which indicates a change in the structure of the paper. It is not known as yet whether or not a stable structure

can be obtained by preheating to a temperature sufficiently high to include the entire range of measurements, and until this is ascertained the values given are of a tentative nature, although no more so than calculations made by other investigators from sorption data. Figure 8 illustrates the heat of adsorption for one gram-molecule of water on an infinite quantity of kraft process wood pulp paper containing the quantity α of adsorbed water. The solid parts of the curves are those values which fall within

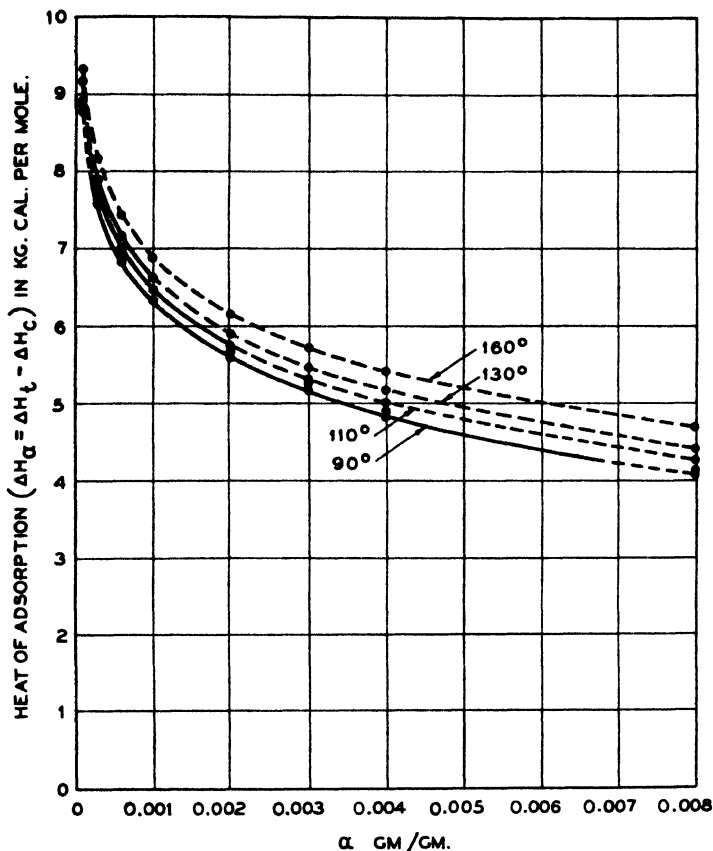


FIG. 8. Heats of adsorption of water on kraft process wood pulp paper

the range of humidities covered, while the dotted portions are extrapolated by means of the equation. The change in heats of adsorption with temperature is small and may not be real, although the increase in the heats with increasing temperatures does not appear unreasonable.

The "heat of adsorption" values are arbitrarily chosen as the differences between the total heats evolved in adsorption and the heats of condensation of water vapor to liquid water. These are the quantities called by

Newsome and Sheppard (4) "heats of wetting." It may be argued that the heat of crystallization of water should be subtracted also, but it is not known in what form comparable to free water the adsorbed water exists, so that any subtraction of heats of crystallization calculated from existing data would be highly questionable, and the variation with temperature is likely small in comparison with the variation in heats of condensation of water with temperature.

Curves for the heats of adsorption of water on the linen rag paper are not shown, as the constants obtained from the isotherms do not appear to be as reliable as those obtained from the kraft paper. It is fairly certain, however, that the slope of the ΔH versus α curve is greater, values of ΔH being substantially higher at moisture contents of 0.001 g. per gram and less, while the values fall off more sharply toward zero at the higher adsorptions.

SUMMARY

1. The apparatus employed to obtain sorption isotherms is described, with particular attention to two methods of measuring the quantity of water admitted to the adsorbent.

2. Adsorption isotherms for water on two types of cellulosic tissue, one of linen derivation and the other of wood pulp, have been obtained for temperatures from 100°C. to 150°C. and for equilibrium water vapor pressures from 0 to 25 mm. of mercury.

3. The Freundlich adsorption equation is found to apply to the isotherms in the range studied. A table of the calculated constants is presented.

4. Hysteresis between adsorption and desorption equilibria is found under the conditions of the experiment, but no quantitative data are presented.

5. Drying paper at temperatures higher than the temperature at which adsorption is subsequently measured is shown to cause a large diminution in the adsorption at the temperature of measurement.

6. Tentative values for the heats of adsorption are calculated by means of a modification of Freundlich's heat of adsorption equation, and curves are presented for the heats of adsorption on wood pulp paper with respect to the quantity adsorbed.

REFERENCES

- (1) DAVIDSON AND SHORTER: J. Textile Inst. **21**, T165 (1930).
- (2) FREUNDLICH: Colloid and Capillary Chemistry, pp. 117-19, 135. E. P. Dutton and Co., New York (1922).
- (3) MURPHY AND LOWRY: J. Phys. Chem. **34**, 598 (1930).
- (4) NEWSOME AND SHEPPARD: J. Phys. Chem. **36**, 3, 930 (1932).

- (5) PIDGEON: Can. J. Research **10**, 713 (1934).
- (6) PIDGEON AND MAASS: J. Am. Chem. Soc. **52**, 1053 (1930).
- (7) SALLEY: Textile Research **5**, 493 (1935).
- (8) SEBORG: Paper presented at meeting of TAPPI, New York, February 21, 1938.
- (9) SEBORG AND STAMM: Ind. Eng. Chem. **23**, 1271 (1931).
- (10) SHEPPARD AND NEWSOME: Ind. Eng. Chem. **26**, 285 (1934).
- (11) SPEAKMAN AND STOTT: J. Textile Inst. **27**, T186 (1936).
- (12) URQUHART: J. Textile Inst. **20**, T125 (1929).
- (13) URQUHART AND WILLIAMS: J. Textile Inst. **15**, T559 (1924).

FURTHER INVESTIGATION OF THE CHAIN STRUCTURE OF LINEAR POLYESTERS¹

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INTRODUCTION

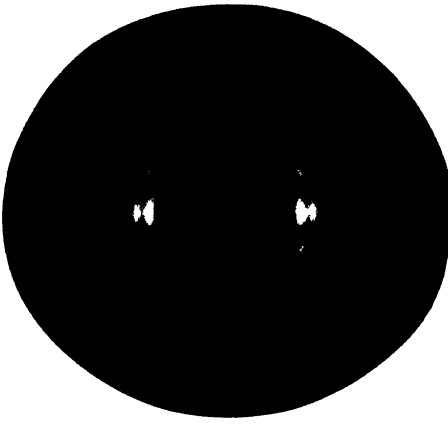
The crystalline or pseudocrystalline nature of high polymers is of profound importance in determining the physical properties of these substances. Because of their polycrystallinity, however, the information that can be deduced concerning their crystalline structure from x-ray studies is limited. Lack of definite information regarding the chemical structures of many of the compounds heretofore investigated has further complicated this problem. By the examination of a number of closely related compounds of known chemical structure this latter difficulty is avoided, and at the same time an added advantage is provided by the progressive changes that are known to occur in homologous series.

In a previous paper (5) certain general features of the x-ray diffraction patterns of a number of linear polyesters of known chemical constitution were considered. It was shown that oriented fibers of these compounds produce sharp x-ray fiber patterns, which are characteristic of the chemical repeating unit present. It was also pointed out that the long-chain molecules in some of these compounds conform closely to a planar zigzag arrangement of the chain atoms, whereas in others a helical or folded form of chain was required in order to explain the experimental results.

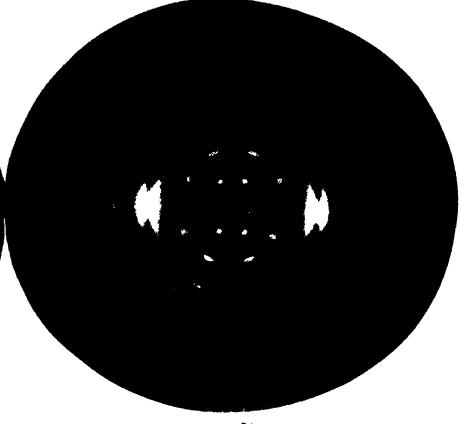
It is the aim of the present paper to present systematically the data now available on the ethylene series of polyesters and to reinterpret the results on the basis of new information. In doing this, use is made of the older data as well as of recent results on polyethylene sebacate. Data on the polymeric self-polyester of ω -hydroxydecanoic acid are also considered with the results on the ethylene compounds. This ester possesses a particularly simple chain constitution and is most conveniently treated at this time.

The methods employed for preparing the compounds and the x-ray technique employed will not be given here, since details are available in

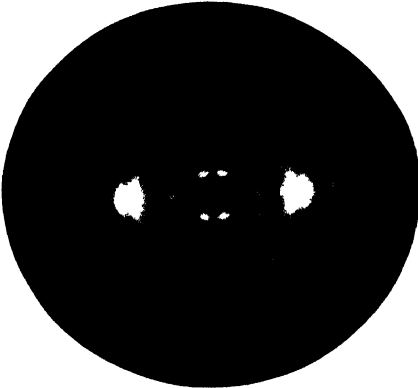
¹ Presented at the Fifteenth Colloid Symposium, held at Cambridge, Massachusetts, June 9-11, 1938.



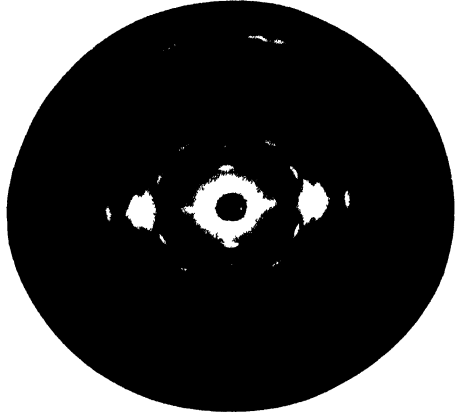
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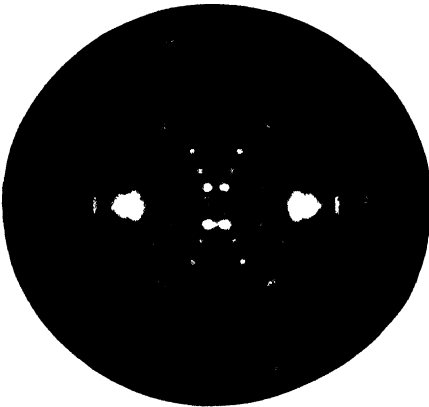
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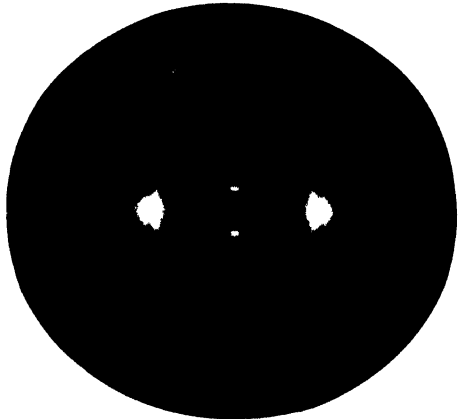
C



D



E



F

FIG. 1 (see facing page for legend)

other publications (2, 5). It should be mentioned, however, that in the present work efforts have been made to improve the accuracy of measurement of the specimen-to-plate distance by automatic standardization with sodium chloride. This was done by dusting the fiber bundles with the finely divided salt (1). The results so obtained were found to agree with those previously reported to within the experimental error (approximately 1 per cent).

COMPOUNDS STUDIED

In order to secure data on other members of the ethylene series than those which were studied in the previous work, attempts were made to prepare polyethylene oxalate, malonate, glutarate, and suberate. Only in the last case, however, was it found possible to secure a product suitable for x-ray investigation. The polymeric self-ester of ω -hydroxydecanoic acid was prepared from the pure acid² by heating for several days in a stream of pure nitrogen gas at 200°C. Both of the polyesters had average molecular weights greater than 15,000, as measured by viscosity methods, and could be cold drawn readily into highly oriented fibers suitable for x-ray investigation (2).

RESULTS

The x-ray fiber patterns corresponding to the ethylene polyesters that have been prepared to date are given in figure 1 (A to E). Figure 1F shows the pattern obtained from the self-ester of ω -hydroxydecanoic acid. Under each photograph is given the formula of the chemical repeating unit, together with the observed identity period as obtained from the fiber diagram and the value of this period calculated on the assumption of a planar zigzag chain. The identity periods for the succinic, adipic,

FIG. 1. Fiber patterns of the polyesters

<p>A. Polyethylene succinate $\text{—O(CH}_2\text{)}_2\text{OCO(CH}_2\text{)}_2\text{CO—}$ I (calculated) = 9.70 Å. I (observed) = 8.32 Å.</p>	<p>B. Polyethylene adipate $\text{—O(CH}_2\text{)}_2\text{OCO(CH}_2\text{)}_4\text{CO—}$ I (calculated) = 12.21 Å. I (observed) = 11.71 Å.</p>
<p>C. Polyethylene suberate $\text{—O(CH}_2\text{)}_2\text{OCO(CH}_2\text{)}_6\text{CO—}$ I (calculated) = 14.73 Å. I (observed) = 14.1 Å.</p>	<p>D. Polyethylene azelate $\text{—O(CH}_2\text{)}_2\text{OCO(CH}_2\text{)}_7\text{O—}$ I (calculated) = 32.0 Å. I (observed) = 31.5 Å.</p>
<p>E. Polyethylene sebacate $\text{—O(CH}_2\text{)}_2\text{OCO(CH}_2\text{)}_8\text{CO—}$ I (calculated) = 17.24 Å. I (observed) = 16.83 Å.</p>	<p>F. Poly-ω-hydroxydecanoate $\text{—O(CH}_2\text{)}_9\text{CO—}$ I (calculated) = 27.30 Å. I (observed) = 27.1 Å.</p>

² The authors are indebted to Mr. W. S. Bishop for the preparation of the pure acid.

TABLE 1
Interplanar spacings and fiber periods of polyesters

REFLECTION	POLYTETYLENE SUBSTRATE			ω -HYDROXYDECANOIC ESTER		
	$d(\text{\AA})$	I^*	Intensity†	$d(\text{\AA})$	I	Intensity
A ₁	4.11		VS	4.17		VS
A ₂	3.61		VS	3.73		VS
A ₃	2.93		S	2.99		M
A ₄	2.49		M	2.49		M
A ₅	2.38		W	2.36		VW
A ₆	2.17		S	2.22		S
A ₇	2.06		W	2.08		M
I ₁	12.60	13.8	VS			
I ₂	6.30	13.8	W			
I ₃	2.66	(14.8)	VW			
II ₀				13.40	26.8	VS
II ₁	6.45	14.2	S			
II ₂	4.08	13.8	W			
II ₃	2.93	14.1	VW			
II ₄	2.43		VW			
III ₁	4.27	14.1	W			
III ₂	3.68	14.1	S			
III ₃	2.78	14.2	W			
III ₄	2.51	13.8	W			
IV ₀				6.65	(26.6)	VW
IV ₁	3.19	14.2	M			
IV ₂	2.53	14.1	W			
V ₁	2.57	14.1	M			
V ₂	2.35	14.1	M			
V ₃	2.21	14.1	W			
VI ₀	(2.28)?	(13.7)	M	4.47	26.8	W
VI ₁	2.12	14.2	VS			
VI ₂	2.00	14.2	M			
VI ₃	1.85	14.1	M			
VIII ₀				3.33	(26.6)	VW
XI ₁				2.21	26.9	VS
XI ₂				2.11	27.3	M
XI ₃				2.06	27.2	M
XI ₄				1.92	27.2	M
XI ₅				1.75	27.4	W
Mean fiber period ..		14.1 \pm 0.05			27.1 \pm 0.1	

* I = identity period.

† V = very; W = weak; S = strong; M = moderate.

and azelaic esters are those previously published (5). For the sebacic ester recent measurements favor the value $16.83 \pm 0.05 \text{ \AA}$., which is somewhat higher than that previously reported. The results of the measurements on the suberic and ω -hydroxydecanoic esters are given in table 1, in which the conventional way of designating the reflections has been followed. The corresponding measurements on the other esters have been given previously (5).

INTERPRETATION OF RESULTS

A. The fiber periods

From figure 1 (A to F) it is evident that the succinate ester, the lowest member of the series which has been prepared in suitable form for study, shows a decidedly different pattern from the succeeding esters. This has been interpreted (5) as indicative of a coiled or helical form of chain molecule, since the observed identity period in the fiber direction is much too short to be explained in any other way. The other esters in figure 1 agree well with a planar zigzag form of chain. As the comparative values below each photograph show, however, the observed periods appear to be definitely shorter than those calculated on the assumption of $C-C = 1.54 \text{ \AA}$., $C-O = 1.43 \text{ \AA}$., and the tetrahedral angle (13). Neglecting the possibility that a constant error may be present,³ we must assume either that the chains deviate slightly from the zigzag arrangement or that the bond distances or angles deviate from those employed in the calculation.

Some additional information on this point is furnished by figure 2, which is a plot of the calculated and observed lengths of the chemical repeating units against the number of atoms in these units. Since the observed increase in length per chain atom as calculated from the slope of the line drawn through the esters other than the succinate is 1.27 \AA . per added CH_2 group, there is good evidence that the hydrocarbon portions of the acids conform to the planar zigzag arrangement (8). This would require that any difference occur in the glycol portion of the ester either as a deviation from the planar form or as a deviation in the oxygen bond angle. A bond angle of approximately 70° would account for the observed differences. In this connection it is interesting to note that the polyester of ω -hydroxydecanoic acid agrees with the calculated value within the allowable experimental error, indicating that the former explanation of the shortening is the more reasonable one.

Figure 2 likewise furnishes confirmation of the idea that the chains of the polyesters lie parallel to the axis of the fibers drawn from them. This

³ Electron diffraction measurements on the adipate and sebacate esters by K. H. Storks (12) also show lower values of the identity period than those calculated.

follows from the fact that the observed increase in chain length per CH_2 group in this direction is in almost exact agreement with that calculated.

B. Crystalline structure of the polyesters

The sharpness of the fiber patterns for the esters (figure 1) shows that in spite of their high molecular and polydisperse nature they are to be regarded as highly crystalline substances. Furthermore, the agreement of the observed fiber periods with the lengths of the chemical repeating units as calculated from their structures proves that it is the latter which

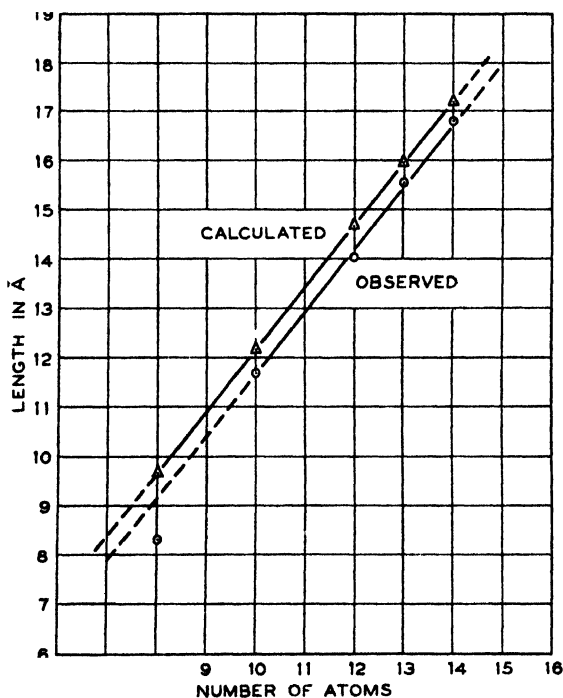


FIG. 2. Lengths of the chemical repeating units plotted against number of chain atoms for the ethylene polyesters

function as the units of packing. This is in contrast to the lower molecular esters (10), acids (11), and paraffins (8), in which the molecule is the packing unit. There is a striking similarity, however, between the x-ray diffraction patterns of high and low molecular chain compounds, as will be apparent from what follows.

If the x-ray measurements on the polyesters (excluding the succinate) are compared with those deduced by Müller (8) for the paraffin $\text{C}_{29}\text{H}_{60}$, a striking resemblance is apparent. Table 2 shows the interplanar spacings of these esters for planes parallel to the fiber axis, along with the

spacings calculated from Müller's model. The recent results of Kohlhaas (7) on cetyl palmitate have also been included. It is evident from the agreement that the same type of packing of the chains is present in all of these long-chain compounds. It appears, therefore, that, insofar as the reflections from these planes are concerned, it makes little difference whether the crystal units are joined by primary valences or simply by association forces.

It has been found possible to account for all of the reflections observed in the fiber patterns of polyethylene azelate and in poly- ω -hydroxydecanoate on the basis of the orthorhombic cell proposed by Müller (8), where the observed fiber periods are substituted for c in each case.⁴ For these esters the dimensions of the orthorhombic cells are $a = 7.45 \text{ \AA.}$, $b = 4.97 \text{ \AA.}$, and $c = 31.2 \text{ \AA.}$ or 27.1 \AA. for the azelate and decanoate,

TABLE 2
Comparison of interplanar spacings in the zone of chain axis

COMPOUND	SPACING IN ÅNGSTRÖM UNITS						
	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇
Polyesters:							
ω -Hydroxydecanoate	4.17	3.73	2.99	2.49	2.36	2.22	2.08
Ethylene adipate	4.13	3.62	2.94	2.52	2.35	2.18	2.09
Ethylene suberate	4.11	3.61	2.93	2.49	2.38	2.17	2.06
Ethylene azelate	4.17	3.70	2.97	2.49	2.36	2.21	2.08
Ethylene sebacate	4.17	3.70	2.97	2.51	2.36	2.19	2.08
Paraffin:							
C ₂₂ H ₄₆ (Müller)	4.13	3.73	2.99	2.49	2.36	2.22	2.07
Ester:							
Cetyl palmitate (Kohlhaas)	4.099	3.711					

respectively. Simple calculation also shows that the number of chemical repeating units per unit cell on the basis of the observed densities of 1.172 and 1.064, respectively, is 3.84 and 3.80, which is in close agreement with the expected value of 4.0. It is not possible, however, to account for all of the observed reflections in the case of the other polyesters on this same basis. Thus, in the adipate, suberate, and sebacate polyesters there are present pyramidal planes of large spacings, which require unit cells considerably larger than that of Müller.

In order to obtain a truer picture of the situation, let us examine the fiber patterns of figure 1 more closely. Several important facts are immediately evident:

(1) The polyesters that contain an odd number of chain atoms possess

⁴ This agreement, of course, does not prove that these esters necessarily have this structure.

a twofold screw axis on the basis of a planar zigzag structure. The presence of strong meridian reflections on the second layer-lines of the fiber patterns of these esters (figure 1, D and F) proves that the screw axis of the chain is communicated to the crystal lattice itself, and that the repeating units line up with the terminating and median $\text{C}=\text{O}$ groups in planes which are perpendicular to the fiber axis. These planes are represented by the horizontal lines in figure 3b. For the even esters, on the other hand, the strong reflections due to the fiber periods occur on the layer-lines corresponding to the number of chain atoms in the chemical repeating units in each case.⁵ In order to explain this result we are forced to assume that, although the carbon atoms of the various chains in the

PROJECTION PERPENDICULAR TO FIBER DIRECTION

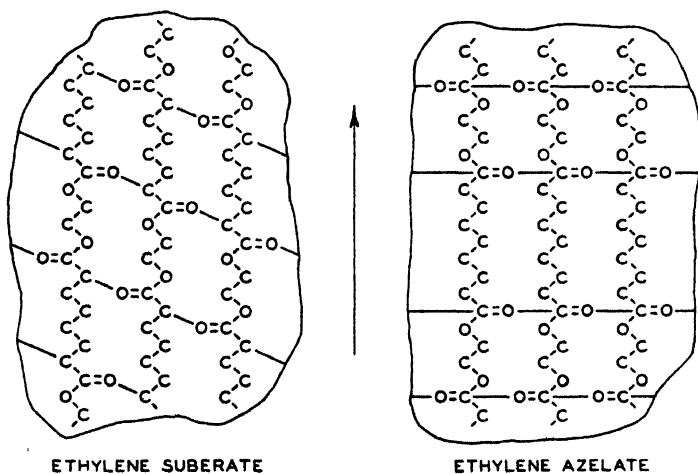


FIG. 3. Diagrammatic projection taken perpendicular to the chain direction for the even (a) and odd (b) polyesters

crystals of these esters fall in horizontal planes, the corresponding $\text{C}=\text{O}$ groups of successive chains must be displaced along the chain direction with respect to one another so as to fall in planes which are inclined to the fiber direction. This is verified for the even esters by the appearance of strong first-order reflections from pyramidal planes. These reflections are apparent in B, C, and E of figure 1 near the primary beam.

(2) Of particular interest is the strong reflection that occurs just off the meridian line on all of the patterns of figure 1 with the exception of the succinate. This reflection is present whether the ester under consideration is even or odd and always falls on the layer-line corresponding to one-

⁵ This is not evident from the x-ray patterns, but is shown by electron diffraction patterns taken by K. H. Storks (12).

half the number of chain atoms present in the x-ray repeating unit. This immediately suggests that the plane corresponding to this reflection makes an angle with the fiber axis such that two atoms of each chain are included (or nearly included) in it. This plane is represented by the inclined parallel lines in figure 3a. The fact that the common spacing (2.13 Å.) of these planes is greater than the C—C bond distance proves that they lie at an angle to the fiber axis which is greater than that formed by the C—C bond with this axis ($35^{\circ} 15'$).

As mentioned above in the case of the adipate, suberate, and sebacate esters (figure 1 B, C, and E), both the reflection under discussion corresponding to the spacing 2.13 Å. and those corresponding to low-order reflections from pyramidal planes of large spacings are observed. A consideration of these various spacings shows that the former may be regarded as the $N/2$ orders of the latter reflections, where N represents the number of chain atoms in the x-ray repeating unit in each case. This suggests not only that the chain carbon atoms fall in planes inclined to the fiber axes but also that the carbonyl oxygen atoms fall in these planes. As stated previously, high intensities of the first-order reflections from these planes are in agreement with an arrangement shown diagrammatically in figure 3a, in which the carbonyl groups of adjacent chain molecules are shifted uniformly an integral number of chain atoms with respect to one another. The amount of this shift has not been definitely determined and is not necessarily two carbon atoms as shown in figure 3a. The absence of lower orders of reflection from the meridian planes is in further support of this view. A more quantitative treatment of the intensities of the various fiber diagrams of these compounds must await the investigation of other members of the polyester class.

(3) The occurrence of the first-order reflection of these pyramidal planes has another important result. It introduces large spacings which it is impossible to index on the basis of the simple model of Müller, which served for the odd esters. Since the equality of the spacings of the planes of the zone of the chain axis indicates that the chains must be packed together laterally in the same manner as for the paraffins, the shift of the molecules along their lengths offers a convenient way of accounting for the increase in the cell dimensions without the necessity of changing the orientation of the chains in azimuth. It has been found by the application of graphical methods that the crystal system of the even esters of figure 1 is in all probability monoclinic, in which the chain axes are perpendicular to the monoclinic base. The cell dimensions, however, are not those proposed previously by Fuller and Erickson (5), since the present results indicate that the cell increases progressively in two dimensions as we ascend the series. Furthermore, the type of cell found to apply to cetyl palmitate by Kohlhaas (7) and to stearic acid by Germer and Storks

(6) does not apply here, since the chain molecules in these cases do not lie perpendicular to the cell base.

We shall not attempt to go into the details of the molecular arrangement at this time, since a later publication will treat this subject. The general features of the crystalline structure of the polyesters, however, will be apparent from the above discussion.

C. Polymorphism in the polyesters

The x-ray results so far reported on the polyesters have been obtained at room temperature. In view of the transitions that occur in the crystalline structures of the paraffins (9) and stearic acid (3) under certain conditions, it might be expected that such transitions would be observed also in the case of the polyesters. That this is the case is shown by the occurrence of two sets of equatorial reflections in one photograph obtained on the ethylene succinate polyester. The occurrence of the two forms has

TABLE 3

Measurements of the equatorial spacings of polymorphic forms of polyethylene succinate

FORM	SPACING IN ÅNGSTRÖM UNITS					
	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆
A-form.....	5.37	4.41	3.85	3.12	2.70	1.92
B-form.....	4.12	3.57	2.92			

not been observed in any of the other fiber diagrams that have been taken. This erratic behavior has been observed by Germer and Storks (6) in the case of stearic acid and by Fuller (4) in the case of gutta-percha. To the authors' knowledge, this is the first time polymorphism has been observed in a synthetic polymeric compound.

Table 3 gives the results of the measurements of the equatorial spacings. It is evident from this table and from table 2 that the second form of the succinate (B-form in table 3) corresponds to the lattice spacing that is characteristic of the other ethylene esters. It is therefore logical to conclude that the new crystal form represents a transition from the helical to the planar (or nearly planar) zigzag type of chain. Unfortunately, the new form is too weak in intensity to allow observation of any of the layer-line reflections from this modification, so that it cannot be determined whether or not the expected expansion in the fiber direction has occurred. Further study of the phenomenon will be necessary before definite conclusions in this regard can be drawn.

SUMMARY

1. From a study of the fiber patterns obtained on oriented fibers of the ethylene polyesters of succinic, adipic, suberic, azelaic, and sebacic acids and the self-polyester of ω -hydroxydecanoic acid it has been shown that, with the exception of the succinate ester, the polyesters conform essentially to a planar zigzag type of chain structure in which the chains lie along the fiber axis. A comparison of the fiber periods calculated on this basis with those observed indicates that a slight shortening from the planar form of chain exists. Evidence favors the view that such shortening occurs in the glycol portions of the esters, either because of a deviation from the planar configuration or because of a decrease in the oxygen valence angle. In the case of the succinate ester it has been found that two crystalline forms are possible. In one form (the usual one) the molecules appear to possess a helical configuration. The second form corresponds to that observed in the case of the other esters, in which the chain molecules are essentially planar zigzag in structure.

2. The crystals of the polyesters that correspond to the planar zigzag chain configuration have been found to have many points in common with the low molecular long-chain compounds. In particular, the polyesters containing an odd number of chain atoms in the repeating unit are found to conform to the same unit cell as has been found for $C_{29}H_{60}$, except for the c dimension. For these odd polyesters the ends of the chemical repeating units of adjacent chains are arranged in planes perpendicular to the fiber axis.

3. In the case of the polyesters that contain an even number of chain atoms in the repeating unit, the simple orthorhombic cell above is not satisfactory. The appearance of reflections from pyramidal planes of large spacing in the fiber patterns of these even esters favors an arrangement in which the repeating units in neighboring chains are shifted along the fiber direction with respect to one another so that the terminating $C=O$ groups fall in these planes.

4. The appearance of the first-order reflections from the pyramidal planes mentioned in the preceding paragraph requires considerably larger unit cells for the even esters. Present evidence favors monoclinic cells for these esters, in which the chain molecules lie along the orthogonal axis of the cell. The cell previously suggested by Fuller and Erickson, however, is not correct, since the different esters require cells which are of different size in the plane perpendicular to the fiber axis.

REFERENCES

- (1) CLARK, WALTHIUS, AND SMITH: *Rubber Age* **42**, 35 (1937).
- (2) CAROTHERS AND HILL: *J. Am. Chem. Soc.* **54**, 1579 (1932).

- (3) DUPRÉ LA TOUR, F.: J. phys. radium **8**, 125 (1937).
- (4) FULLER, C. S.: Ind. Eng. Chem. **28**, 907 (1936).
- (5) FULLER AND ERICKSON: J. Am. Chem. Soc. **59**, 344 (1937).
- (6) GERMER AND STORKS: J. Chem. Phys. **6**, 280 (1938).
- (7) KOHLHAAS, R.: Z. Krist. **98**, 419 (1938).
- (8) MÜLLER, A.: Proc. Roy. Soc. (London) **120A**, 437 (1928).
- (9) MÜLLER, A.: Proc. Roy. Soc. (London) **138A**, 514 (1932).
- (10) MÜLLER AND SHEARER: J. Chem. Soc. **123**, 3156 (1923).
- (11) PIPER, S. H.: J. Chem. Soc. **1929**, 234.
- (12) STORKS, K. H.: J. Am. Chem. Soc. **60**, 1753 (1938).
- (13) SUTTON AND BROCKWAY: J. Am. Chem. Soc. **57**, 473 (1935).

SKIN REACTIONS. VII

RELATIONSHIP OF SKIN PERMEABILITY TO ELECTROPHORESIS OF BIOLOGICALLY ACTIVE MATERIALS INTO THE LIVING HUMAN SKIN¹

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INTRODUCTION

In the fields of allergy and dermatology the chemical bases of skin reactions are playing an increasingly significant rôle. The complicated colloid system of the skin offers to those interested in the mechanisms of skin reactions a tissue to which the principles of surface chemistry and physics may be successfully applied. In man the living skin is readily accessible to various types of investigative procedures. Thus the study of the hypersensitiveness of the skin to specific proteins like that of rag-weed pollen very frequently mirrors the sensitiveness of the entire organism, as evidenced by the presence of special antibodies in the blood stream.

Foremost among the problems of skin physiology in relation to therapeutics is the problem concerned with the absorption of drugs through the intact skin. Drugs are usually applied to the skin for both local and general effects in the form of ointments, dependence being made upon forces resulting from diffusion and solubility. These methods when used alone are limited by their slowness and the requirement of complicated vehicles to make them feasible at all. A method of great usefulness in accelerating the introduction of substances into the intact skin is that employing the galvanic current. A piece of absorbent material, like cotton, is wet with a solution of the substance and applied to the skin. The subject is placed in the galvanic circuit as indicated below:

metal	cotton and	skin	body	skin	cotton and	metal
elec-	substance to				saline	elec-
trode	be introduced					trode

In general, current densities up to 0.5 milliampere per square centimeter for the positive pole and 0.3 milliampere for the negative cause insig-

¹ Presented at the Fifteenth Colloid Symposium, held at Cambridge, Massachusetts, June 9-11, 1938.

nificant trauma and no discomfort. It is evident that this method, commonly called electrophoresis or iontophoresis (erroneously termed "ionization" (3)) embodies certain advantages in both experimental and therapeutic procedures. (1) The surface of the skin is unbroken. (2) The current density may be varied over a wide range. (3) Areas differing in size from that of a hair follicle to that of very large surfaces may be studied. (4) The total amount of material introduced and the rate of introduction can be varied by varying both the current density and the concentration. (5) There is excellent uniformity in the distribution of the drug through the skin compared, for example, with that obtained by injection. (6) The skin may act as a reservoir.

NATURE OF THE SKIN

The outer layer of living human skin may be considered to be a membrane, consisting of very fine pores which lead from the surface toward the vascular regions below. All the experimental evidence to be presented can be qualitatively explained on the assumption of a fairly rigid inanimate system. Actually, of course, the pores may change their entire nature under the influences of the electrophoretic procedures employed, as well as with changes in the physiological state of the individual during the course of an experiment. A quantitative treatment of electrophoresis through the skin will not be possible until these physiological factors are better understood, but these factors appear to be of secondary importance for the qualitative considerations to be examined.

It is evident that if the skin is considered to be a pore-like membrane it would differ fundamentally from a wet collodion membrane when the skin pores are incompletely filled with liquid. Either a gel-like or a pore-like membrane would allow highly diffusible substances to pass readily through it when the inside and outside surface are in contact with fluid. On the other hand, under the same circumstances, a pore-like membrane which contains air spaces of small diameter and is otherwise permeable with difficulty will not readily allow diffusion. Actually, of course, the outer skin layer may be a combination of the two types. If it is, the pore-like part must constitute the outermost layer.

When an electrical potential is applied across a membrane of this nature, the inner and outer surfaces being in contact with fluid, electro-osmotic forces would tend to displace the air in the pores with fluid. The pores would then contain an unbroken column of conducting fluid in which would be displayed all the phenomena of electrokinetics. Ions would be forced through by the potential drop (iontophoresis or ionic migration), and the columns of liquid as a whole would move either toward the inside or toward the outside depending upon conditions (electroösmosis).

Besides these two phenomena, diffusion must be considered, for, when a current is passing, diffusion can take place through the continuous columns of liquid established. If electrophoresis and electroösmosis are in the same direction or one is much larger than the other, the diffusion term may be neglected in qualitative considerations. However, under certain circumstances the electrophoretic and electroösmotic velocities may be of the same order of magnitude and opposite in sign. For these cases the diffusion term must be considered. Shortly, diffusion velocities will be calculated and an example given in which the diffusion term may be of importance.

SIMPLE CASE OF IONTOPHORESIS: HISTAMINE HYDROCHLORIDE

The drug histamine is of great importance in skin reactions. When it is introduced into the vascular regions of the skin, the whealing reaction occurs; the skin becomes elevated and resembles a hive or mosquito bite in the zone of pharmacological action. This reaction is very similar to the one obtained in certain allergic individuals when substances to which they are sensitive are introduced into the skin.

Histamine (imidazoleethylamine) is a readily diffusible diacidic base (8), with a first dissociation constant about the same as that of ammonia and a second very much weaker. Below pH 4.0 the doubly charged ion, histamine⁺⁺, predominates in aqueous solution. From pH 4.0 to pH 10 histamine(OH)⁺ predominates, while above pH 10 solutions of the drug contain mostly the uncharged form, histamine(OH)₂. Abramson and Alley (3) have recently made a careful study of the electrophoretic introduction of histamine into living human skin. They found that in the absence of other electrolytes water solutions of histamine salts in dilutions as high as 1:5,000,000² gave a whealing response when the positive pole was applied to the cotton containing the histamine. They used a constant current density and time interval,—0.5 milliampere per square centimeter for 5 min. In no case was a reaction ever obtained with the negative pole. The method is so sensitive that Abramson and Ochs were able to work out a semi-quantitative procedure for determining minute amounts of histamine in complicated media, e.g., whole blood (5).

The effect of salts at constant current density was carefully studied (see table 2 of reference 8). They found that, as the concentration of potassium chloride was increased, larger concentrations of histamine were necessary to produce a reaction. In 2.4 *M* potassium chloride practically no reaction was obtained with the most concentrated histamine solution employed (1:5000). The authors explained their findings by pointing

* With subsequent development of technique histamine in higher dilutions has been detected.

out that as the inert salt concentration increases the fraction of the current carried by the histamine decreases, and therefore that the amount of histamine electrically transported into the skin decreases.

Further evidence that the galvanic introduction of histamine may be considered to be a simple case of iontophoresis was furnished by Abramson, Engel, Lubkin, and Ochs (4). These authors observed that histamine which had previously been electrically introduced into the skin with the positive pole could be partially removed by reversing the current. Quantities of histamine large enough to cause strong reactions in a new area of skin were successfully recovered with the negative pole (within 40 min.) from the treated area into a piece of cotton wet with distilled water. This type of wheal produced in a new area of skin after recovery of histamine we shall call a *transferred wheal*.

Unpublished results of the writers on the iontophoresis of histamine demonstrate further the pore-like nature of the outer skin membrane. It was discovered that when the positive pole was applied to a piece of cotton, wet with distilled water, over an area to which histamine had previously been applied by electrophoresis, the whealing reaction reappeared. This type of wheal produced at the primary site of histamine iontophoresis we shall call a *secondary wheal*. Thus wheals, the severest of which last only a few hours, were caused to reappear, in some instances as long as five days after the electrical introduction of histamine. Furthermore, if the negative pole was applied to an area which had previously received histamine electrically, in some instances as long as four days, and invariably 24 hr. after the original application, histamine could be demonstrated in the cotton by the production of transferred wheals. As yet our attempts to remove histamine with the negative pole from an area to which it had been administered by ordinary intradermal injection have failed. Nor has it been possible to cause, with the positive pole, the reappearance of a histamine wheal (secondary) that had been produced by ordinary intradermal injection. In a few experiments in which the histamine had been *pricked* into the skin, the histamine being applied only to the most superficial layers of the skin by this method, it was possible to demonstrate the presence of histamine in the skin 24 hr. later, and occasionally after a longer period, by both secondary and transferred wheals. It appears, therefore, that the intradermal injection method distributes histamine primarily to the deeper layers of the skin, where fewer barriers to diffusion exist.

There must be, then, regions in the skin through which histamine can be readily transported electrically, but with difficulty by diffusion. The pore-like membrane postulated above has such properties, for, when the current is started, the pores will fill by the outward electroosmotic flow of skin fluid or by the inward movement of cotton fluid. The liquid that

fills the pores while the current is flowing will be partially trapped and therefore remain in the skin for long periods. The pores, under these conditions, act as reservoirs from which histamine is released only very slowly.

The capacity of the skin to act as a reservoir for biologically active materials may be connected with the origin of some skin diseases. On the other hand, galvanic therapy might prove useful in removing depots of toxic materials formed in the skin pores, or valuable for establishing depots of materials of therapeutic import in the cases in which slow absorption is desirable, as in all types of vaccination.

ELECTROÖSMOSIS

Electroösmosis through animal tissues was first observed by Porret in the early part of the nineteenth century. In 1860 Kuhne (7) apparently observed electroösmosis in muscle. Roeber, in 1896, investigated the relationships between the field strength and the volume of liquid transported through the skin of the cow. He found that the volume of liquid transported was proportional to the field strength. Morton (9) found that electroösmosis was responsible for the transfer of many substances into the skin and into the pulp of the tooth. In fact, he noted explicitly that solutions of cocaine were more effective in producing anesthesia when applied by electrophoresis if an alcoholic rather than an aqueous medium was employed. Rein (10) emphasized and clarified to some extent the importance of electroösmosis, but some of his conclusions regarding the sign of the charge and the electrophoresis of ions through the pores do not seem to be completely borne out by more detailed experimentation.

The direction of electroösmotic flow in a pore-like membrane depends upon the sign of the average charge on the walls of the pores (2). If the walls are positively charged the solution will move toward the positive pole, and if negatively charged toward the negative pole. In the case of the human skin it is assumed that the walls of the pores are lined with proteins. It is well established that for protein surfaces the charge density at the protein-water interface depends primarily upon the pH of the solution and closely parallels the charge density calculated from the excess of hydroxide or hydrogen ions as determined by titration curves for individual molecules of the same species (1). Therefore the direction of electroösmotic flow in the skin will reverse at the isoelectric point of the pores. According to Rein, the pores of the skin behave as if they are lined with keratin, with an isoelectric point between pH 3.0 and 4.0. At pH values above 4.0, then, the positive pole at the cotton should cause electroösmotic flow into the skin.

The introduction of histamine at pH 12 and of alkaline alcoholic solu-

tions of local anesthetics furnishes examples in which electroösmosis probably predominates. In both of these cases the material successfully introduced is essentially uncharged. There are no examples available for electroösmosis into the skin with the negative pole on the acid side of the assumed isoelectric point of the pores.

For optimum electroösmotic velocity several conflicting factors must be taken into consideration. Thus, the charge depends upon the distance from the isoelectric point. However, increasing the pH generally necessitates increasing the total strength of the solution. High ionic strength slows up electroösmosis in two ways: (1) The potential gradient in the pores, at constant current density, is low because of the high conductivity of the solution in the pores. (2) The ζ -potential of the pores at constant charge density may be reduced.

Abramson and Alley have demonstrated the effect of salts in the case of the electrophoresis of histamine at pH 12. Under these conditions less than 0.1 per cent of the histamine molecules are charged. Yet solutions as dilute as those in the case of histamine hydrochloride mentioned above caused a positive whealing response. The evidence is strong, therefore, that the electrical introduction of histamine at pH 12 is due primarily to electroösmotic forces. Here, as well as with the iontophoresis of histamine salts, it was found that potassium chloride greatly diminished the transport of histamine into the skin.

THE DIFFUSION TERM

The electrical migration of a charged body and the electroösmotic movement of the solution as a whole are strictly additive. The velocity of electrical transport of any charged molecule or particle in a potential gradient will be, then, the algebraic sum of the iontophoretic (electrophoretic) velocity of the particle and the electroösmotic velocity of the solution as a whole,

$$V_e = V_i + V_s \quad (1)$$

where V_e is the resultant velocity due to the electric field, V_i is the velocity the particle would have if the solution as a whole were not moving, and V_s is the electroösmotic velocity of the solution.

In addition, of course, diffusion of the material will occur wherever concentration gradients exist. The diffusion term must be added to equation 1, the complete equation becoming

$$V = V_e + V_d = V_i + V_s + V_d \quad (2)$$

where V is the actual velocity of the molecule or particle and V_d its diffusion velocity.

In general, V_i and V_s are proportional to the potential gradient and

may be complicated functions of the pH and other variable conditions discussed in the foregoing. V_d is proportional to the concentration gradient of the material and may also change considerably with total salt concentration and pH, as well as with the nature of the medium (cell

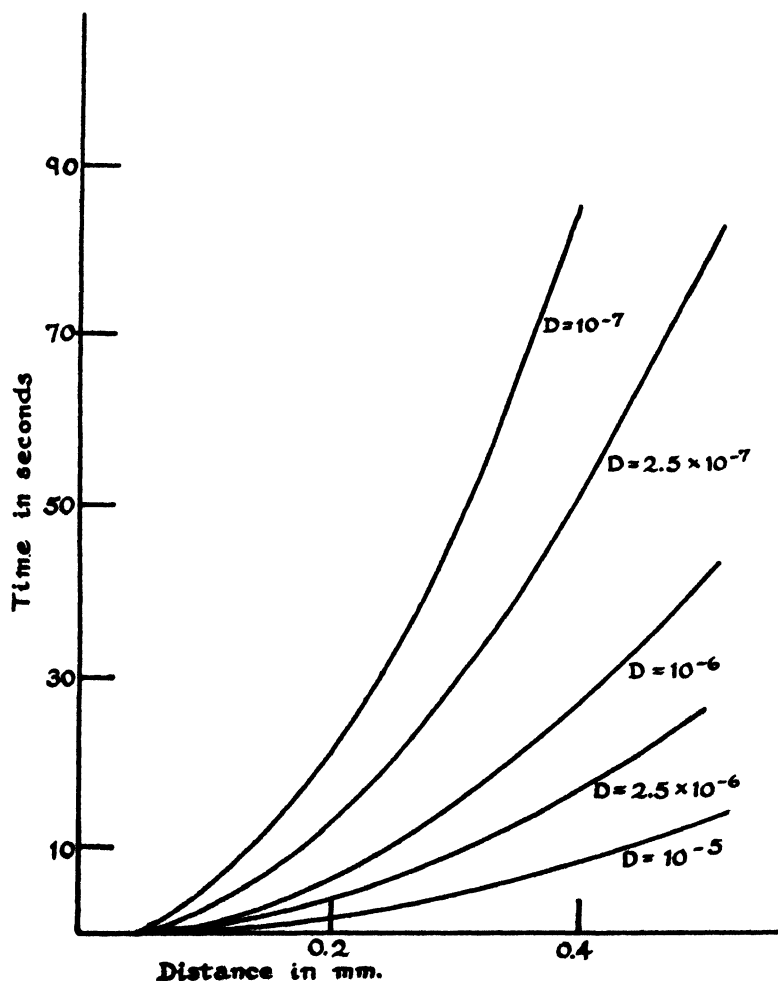


FIG. 1. The time needed for the establishment of a concentration of 1/1000th of the original concentration as a function of the distance from the original boundary.

membranes), although, at least as far as proteins are concerned, V_d changes much less than V_i and V_s as the pH and ionic strength are varied. Since in general V_i and V_s are unrelated, V_d usually operates in the nature of a correction, the magnitude of which cannot be estimated in the general case.

There is, however, one case for which a quantitative treatment is warranted. If the substance to be introduced is a protein and if it is adsorbed by the walls of the pores, it turns out that V_i and V_e can be

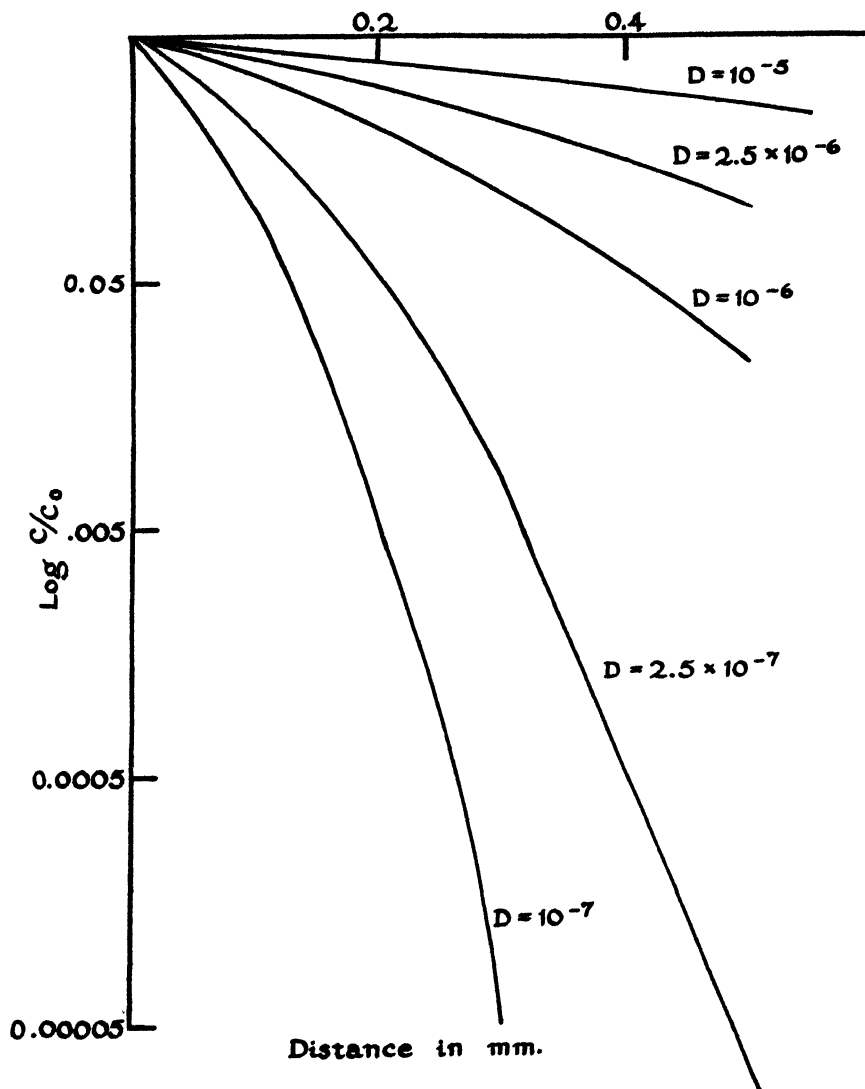


FIG. 2. The concentration ratio C/C_0 as a function of the distances from the original boundary established in 5 min. for various values of the diffusion coefficient.

nearly equal and opposite at all points in the pores, assuming, of course, open pores. If $V_i = -V_e$, equation 2 becomes $V = V_d$, and therefore the problem of calculating V becomes that of calculating V_d . Assuming

cylindrical pores and insensible depletion of the material on the outside of the skin, the equation (6,11,12),

$$C = \frac{C_0}{2} \left(1 - \frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy \right) \quad (3)$$

may be used for calculating diffusion; y is given by the expression

$$y = x/2\sqrt{Dt}$$

C is the concentration, C_0 is the original concentration, x is the distance from the original boundary, in this case the outside of the pores, t is the

TABLE 1

Fraction, C/C_0 , of the original concentration of various substances that would be established at the ends of pores of several lengths in 5 min.

SUBSTANCE	$D \times 10^7$ <i>cm. per second</i>	MOLECULAR WEIGHT	C/C_0			
			0.05 mm.	0.25 mm.	0.5 mm.	1.0 mm.
Egg albumin	9.58	34,000	0.417	0.149	0.0187	0.00000
Serum globulin	5.40	104,000	0.392	0.082	0.0026	
Helix hemocyanin	1.70	4,900,000	0.315	0.008	0.00001	
Histamine acid phosphate	100.00*	210	0.473	0.449	0.260	0.099

* Unpublished value, determined at room temperature, is $(100 \pm 20) \times 10^{-7}$.

TABLE 2

"Average" diffusion velocities, \bar{V} , for $C = C_0/1000$ in microns per second

SUBSTANCE	MOLECULAR WEIGHT	\bar{V} IN MICRONS PER SECOND			
		0.05 mm.	0.1 mm.	0.2 mm.	0.5 mm.
Egg albumin	34,500	36.5	18.2	9.2	3.7
Serum globulin	104,000	20.5	10.3	5.2	2.1
Helix hemocyanin	4,900,000	6.8	3.4	1.7	0.7
Histamine acid phosphate	210	382.0	191.0	85.5	38.2

time, and D is the diffusion coefficient. (See figures 1 and 2 for graphic representation of the theory.)

In table 1 is given C/C_0 at the ends of the pores after 5 min., assuming various values for the length of the pores (length 0.05 to 1.0 mm.), for a series of proteins (molecular weight = 34,000 to 4,900,000) and for an easily diffusible substance, histamine hydrochloride.

It is seen from table 1 that comparatively large concentrations of protein (from an immunological point of view) may be established by diffusion in 5 min. at the ends of pores 0.25 mm. or less in length. Also,

that concentrations of importance physiologically may be established at the ends of pores as long as 0.5 mm., but that if the pores are much longer than 0.5 mm., no important amounts of proteins will reach the ends by diffusion in 5 min.

Histamine (tables 1 and 2) diffuses so rapidly over distances of the order of magnitude of the length of the skin pores (0.1 to 0.2 mm.) that it seems likely that a considerable portion if not most of the histamine, in the case of electrophoresis at pH 12 and even that of iontophoresis of histamine salts, might be carried by diffusion. If so, diffusion explains the great similarity in the action of histamine at pH 12 and of histamine salts.

From a physiological point of view it is interesting to calculate diffusion in another way. The time necessary to establish a concentration, say, 1/1000th of that on the outside of the skin, at the ends of pores of various lengths will be calculated for several proteins by means of equation 3. If C equals $C_0/1000$, equation 3 becomes

$$\frac{1}{1000} = \frac{1}{2} \left(1 - \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-y^2} dy \right)$$

or

$$\frac{-2}{\sqrt{\pi}} \int_0^{\infty} e^{-y^2} dy = 0.998$$

From tables for the probability integral, the value of y for which the integral equals 0.998 is 2.184. Therefore

$$y = \frac{x}{2\sqrt{Dt}} = 2.184$$

or

$$x = 4.368\sqrt{Dt}$$

In table 2 is given x/t , an "average" velocity in microns per second, for several proteins and histamine acid phosphate at various distances, x , from the original boundary.

THE DIFFUSION TERM AND RAGWEED ELECTROPHORESIS

The fact that the active constituent of ragweed extract can be introduced into living human skin by electrophoresis is of paramount importance in considerations of the nature of the outer skin membrane. While the active principle of ragweed pollen has not been isolated, many of its properties have been fairly definitely established. First, the active constituent cannot be removed by dialysis and is therefore of high molecular weight. Secondly, it can be completely removed from aqueous solution by adsorption on quartz surfaces. Thirdly, its biological activity follows

closely that of the protein nitrogen in the solutions, and the active principle can be precipitated by the usual protein precipitants, such as ammonium sulfate. And lastly,³ the active principle is apparently an amphoteric substance negatively charged at pH 7.4. All indications, therefore, point to a protein-like body.

Whether or not the active constituent of ragweed is a protein, the fact that it is a large molecule suggests that the effective diameters of the skin pores are greater than those of Cellophane or collodion membranes and that it might be possible to introduce other proteins into the skin by electrophoresis.

When ragweed extract is introduced into the skin of individuals who are skin-sensitive to ragweed, a reaction somewhat similar to that produced by histamine in normal individuals occurs. It was discovered by one of the authors that dialyzed extracts, pH about 7.6, could be introduced into the skin with current densities of from 0.3 to 0.5 milliamperes per square centimeter. These current densities for 5 to 10 min. caused large wheals in individuals hypersensitive to ragweed extract. No wheals were obtained in normal subjects with ragweed extract, nor did the subjects who were sensitive to ragweed give wheals with current alone. The positive pole produced reactions at least as great as the negative pole, even though the material is probably negatively charged under the conditions employed. An explanation of this phenomenon may be that in the case of ragweed the diffusion term of equation 2 predominates. This term, of course, operates independently of the polarity. Further analysis of the mechanism involved is being conducted through the study of the electrical charge of ragweed extracts by the moving boundary method.

SUMMARY

In connection with a study of the absorption of drugs through the living human skin, the outer skin is considered to be a membrane made up of very fine pores. Under normal conditions these pores are held to be incompletely filled with liquid. It is postulated that, when an electrical potential is applied across the skin, the electroosmotic forces would tend to displace the air in the pores with liquid. The pores would then contain an unbroken column of fluid in contact with liquid on the outside and with the dermal tissues beneath. The phenomena of electrokinetics would be displayed in the pores. For the case of the movement of charged molecules through these pores therefore, three factors, which may be summed up algebraically, operate. The first factor is the simple migration of the ions themselves in an electric field. The second factor is the elec-

³ Unpublished work of Abramson, Sookne, and Moyer on the electrical mobility of microscopic quartz particles covered with a film of adsorbed substances from ragweed extracts.

troösmotic flow of liquid as a whole. The third factor, considered for the first time, is diffusion over small distances. In the special case where the electrophoretic and the electroösmotic movements balance one another the diffusion factor may predominate. The diffusion term is treated semi-quantitatively by a special integrated form of Fick's law which, assuming cylindrical symmetry, permits the calculation of the quantity of materials at small distances from the depot on the outer skin surface and for small fractions of the original amount in the depot itself. Diffusion velocities of even large molecules may exceed velocities due to electrical mobility with the usual field strengths across the skin.

The retardation of diffusion in the skin in the absence of a potential gradient is demonstrated by a newly discovered phenomenon associated with the electrical introduction of histamine, a substance of relatively low molecular weight. It was found that histamine which has been electrically transported into the skin remains in the pores for periods as long as a week. Furthermore, by reversing the current histamine can be readily recovered.

The foregoing theory and experiments are applied to the interpretation and the electrophoresis of protein extracts of ragweed pollen into the skin of individuals hypersensitive to these substances.

In conclusion we wish to express our appreciation for the aid given by Mrs. Margery Engel and Mrs. Henrietta Gettner during the course of these investigations.

REFERENCES

- (1) ABRAMSON, H. A.: *Electrokinetic Phenomena and their Application to Biology and Medicine*, Chap. V. The Chemical Catalog Co., Inc., New York (1934).
- (2) ABRAMSON, H. A.: *Urolog. Cutan. Rev.* **62**, No. 4 (1938).
- (3) ABRAMSON, H. A., AND ALLEY, A.: *Arch. Phys. Therapy, X-ray, Radium* **18**, 327 (1937).
- (4) ABRAMSON, H. A., ENGEL, M., LUBKIN, V., AND OCHS, I.: *Proc. Soc. Exptl. Biol. Med.* **33**, 65 (1938).
- (5) ABRAMSON, H. A., AND OCHS, I.: *J. Lab. Clin. Med.*, in press.
- (6) FURTH, O., BAUER, H., AND PIECH, H.: *Biochem. Z.* **100**, 52 (1919).
- (7) KUHN, W.: *Arch. Anat. Physiol.* **2**, 673 (1860).
- (8) LEVY, M. J.: *J. Biol. Chem.* **109**, 361 (1935).
- (9) MORTON, W. J.: *Cataphoresis*. American Technical Book Co., New York (1898).
- (10) REIN, H.: *Z. Biol.* **84**, 41 (1926).
- (11) STEFAN: *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse* **79**, II, 176 (1879).
- (12) SVEDBERG, T.: In *Alexander's Colloid Chemistry*, Vol. I, p. 838. The Chemical Catalog Co., Inc., New York (1926).

THE DISPERSION OF PROTEIN IN AQUEOUS FORMALDEHYDE SOLUTIONS¹

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The reaction between formaldehyde and proteins is of paramount importance in the development of protein plastics (2), coatings, sizes, adhesives, and fibers. It has been used in these industries as a so-called hardening process for many years.

In processes that employ protein dispersions it has not been found possible to combine the formaldehyde with the protein before use, because they react with each other at a rather rapid rate to cause the formation of a precipitate. Therefore the formaldehyde treatment must be a separate step in the process where it is used. Attempts have been made to simplify such processes by using certain compounds in the protein dispersion that give a delayed formaldehyde reaction, but as yet they have not attained any marked success.

In the early literature on the protein-formaldehyde combination, which has been reviewed by Gortner (5), it has been postulated to be a reaction between the formaldehyde and the free amino groups of the protein.

Many studies have been made on the analogous reaction between formaldehyde and amino acids (6), but even for these simpler systems there has been no general agreement on the structure of the compounds formed. Recently attempts to define the protein-formaldehyde linkage by means of x-ray diffraction studies have been made (4), but up to the present time they have yielded no characteristic pattern.

Because of the desire for obtaining greater water resistance in the above-mentioned protein products and because the formaldehyde reaction appears to be the most promising means of accomplishing this result, a

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² A coöperative organization participated in by the Bureau of Chemistry and Soils and the Bureau of Plant Industry of the U. S. Department of Agriculture, and the Agricultural Experiment Stations of the North Central States of Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin.

preliminary study was made of some of the factors that may be presumed to influence this reaction. The pertinent factors include the concentration of formaldehyde, the hydrogen-ion concentration, and the time of reaction. The change in solubility or dispersibility resulting from formaldehyde treatment of several proteinaceous materials has been determined with respect to hydrogen-ion concentration, and the amount of formaldehyde reacting with the protein has been estimated.

EXPERIMENTAL

Materials

The materials used in the investigation were as follows: soybean meal from which the oil had been extracted with petroleum ether and prepared otherwise as previously described (8); a purified soybean protein prepared by extracting the protein from the oil-free meal with water, precipitating the protein from the water dispersion by electro dialysis, and drying at a

TABLE 1
Analysis of the various protein materials used

MATERIAL	NITROGEN	MOISTURE	ASH
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Soybean oil-free meal.....	7.14	10.50	6.03
Dialyzed soybean protein.....	14.3	6.30	2.06
Hammersten's casein.....	14.5	5.60	1.74
Soybean (alpha) protein (commercial).....	14.0	7.80	2.33
Rennet casein.....	13.4	7.83	8.60
Lactic acid casein.....	13.8	6.55	2.91
Zein.....	14.9	7.15	0.28

temperature of 45°C. or below; a commercial soybean (alpha) protein; Hammersten's casein prepared in this laboratory; a commercial rennet casein; a commercial self-soured casein; and a commercial zein. The moisture, nitrogen, and ash contents of the various samples are given in table 1. All of the samples were ground in a pebble mill to pass through a 100-mesh screen. The formaldehyde and other reagents were of the analytical reagent grade.

Extraction procedure

Two and one-half grams of the sample was shaken for 30 min. with 100 ml. of the dispersing solution, the undispersed matter was removed by centrifuging, and an aliquot of the supernatant solution was taken for the nitrogen determination. The pH of the extract was taken with a portable glass electrode pH meter. A more complete description of the procedure has been given elsewhere (8).

The protein dispersion at different pH values was controlled throughout this work with hydrochloric acid and sodium hydroxide. As the work progressed it was found that the largest factor in controlling the amount of nitrogen dispersed was the relative order of addition of the formaldehyde and the dispersing agent. In general, when the formaldehyde was added to the protein before the acid or base, a very low dispersion of nitrogenous material was obtained. On the other hand, when the dispersing agent was added first, a high dispersion of this material resulted. For the sake of brevity these two procedures will be referred to, hereafter, as methods A and B, respectively.

Concentration

Benedicenti (3) reported that variations in the formaldehyde concentrations up to 5 per cent had no effect on his results. To check this conclusion with respect to protein dispersions and to investigate higher concentrations of formaldehyde, extractions were made on commercial soybean protein by procedure A at three different pH values within the range of pH 4.8 to 11.1 and with the formaldehyde concentration varying stepwise from 0.5 per cent to 40 per cent by weight. These results are presented in table 2. They show that when the formaldehyde concentration is below 5 per cent there is a marked increase in the amount of nitrogen dispersed over that for higher formaldehyde concentrations, but that above this level the variation in concentration is not significant. Since procedure A produced a much greater change in protein dispersion than procedure B, it may reasonably be assumed that formaldehyde concentrations above 5 per cent are not a critical factor for method B. The effects caused by changes in concentration of formaldehyde occurring below 5 per cent are attributed mainly to a chemical reaction between the formaldehyde and protein, while the constancy of the results between 5 per cent and 40 per cent concentrations of formaldehyde is interpreted to mean that there is no significant change in the character of the solvent within this range. Unless otherwise indicated, a formaldehyde concentration of 10 per cent by weight was used for the remaining experiments.

Extraction of soybean proteins

The results of nitrogen extraction for soybean meal and dialyzed protein are given in figure 1. Curves III and VI are the regular pH-nitrogen dispersion data for the meal and dialyzed protein, respectively, and are used for comparative purposes; curves II and V are the results of procedure A, and curves I and IV of procedure B. A plot of the data shows, in general, that addition of formaldehyde to the system after the acid or base causes a displacement of the curves towards lower pH values, and that on the alkaline side of the isoelectric point it tends to increase the

amount of nitrogen dispersed. The results obtained by using method A are quite different. The dialyzed protein, curve V, gives practically a straight line at about 0.7 per cent nitrogen, while curve II, for the soybean meal, rises to a maximum nitrogen extraction of about 50 per cent

TABLE 2

Effect of formaldehyde concentration on dispersion of soybean alpha protein at three different pH values

CONCENTRATION OF FORMALDEHYDE	pH	NITROGEN DISPERSED
<i>per cent</i>		<i>per cent</i>
40	4.8	3.0
	7.2	4.7
	10.0	3.3
30	4.9	2.6
	7.3	3.9
	10.0	2.3
20	5.0	2.3
	7.5	3.5
	10.1	2.6
10	5.2	2.0
	7.6	7.6
	10.5	3.8
5	5.5	2.3
	8.0	7.0
	10.8	7.5
2	5.4	1.0
	7.2	28.6
	11.1	13.4
1	5.5	6.8
	6.8	34.3
	7.3	58.0
	10.6	33.5
0.5	5.0	3.0
	7.0	60.8
	10.8	76.7

on each side of the isoelectric point. The results for the nitrogen dispersion of the commercial soybean protein by the three different methods are given in table 3. They are quite similar to those for the dialyzed protein.

The results for rennet and lactic acid caseins are shown in figure 2 and

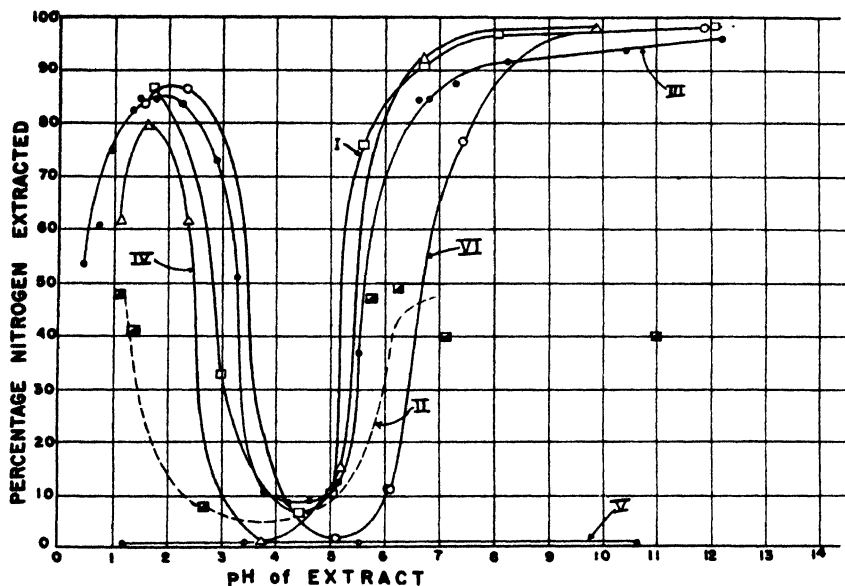


FIG. 1. Effect of formaldehyde on the pH dispersion of soybean meal and purified protein. Curves I (meal) and IV (protein), formaldehyde added after pH dispersion; curves II (meal) and V (protein), formaldehyde added before pH dispersion; curves III (meal) and VI (protein), no formaldehyde.

TABLE 3

Per cent of commercial alpha protein dispersed when pH was varied in the presence or absence of formaldehyde: (A) formaldehyde added before the acid or base, (B) formaldehyde added after the acid or base, (C) without formaldehyde

A FORMALDEHYDE ADDED BEFORE HCl or NaOH		B FORMALDEHYDE ADDED AFTER HCl or NaOH		C HCl or NaOH; NO FORMALDEHYDE	
pH	Nitrogen <i>per cent</i>	pH	Nitrogen <i>per cent</i>	pH	Nitrogen <i>per cent</i>
1.2	1.7	1.2	71.6	1.2	68.7
1.7	1.8	1.4	73.7	1.4	71.5
				1.9	57.8
		2.5	30.7	2.2	42.7
				2.6	25.5
		3.9	2.2	3.2	9.7
5.1	1.5	5.1	8.9	4.1	2.9
		7.1	99.0	5.8	35.8
10.2	2.1			7.4	87.4
				10.1	97.5
				10.9	99.0

are similar in character to the results for the various soybean proteins. From curves I and IV, which represent the regular pH-dispersion data for rennet and lactic acid caseins, respectively, it is evident that rennet casein is more difficult to disperse in the alkaline range than the acid casein. The results for rennet and lactic acid caseins, obtained by method B, are given in curves II and III, from which it is apparent that the presence of formaldehyde causes no substantial change in the dispersion of the acid casein, but that in the case of the rennet casein the presence of formaldehyde results in a displacement of the curve towards lower

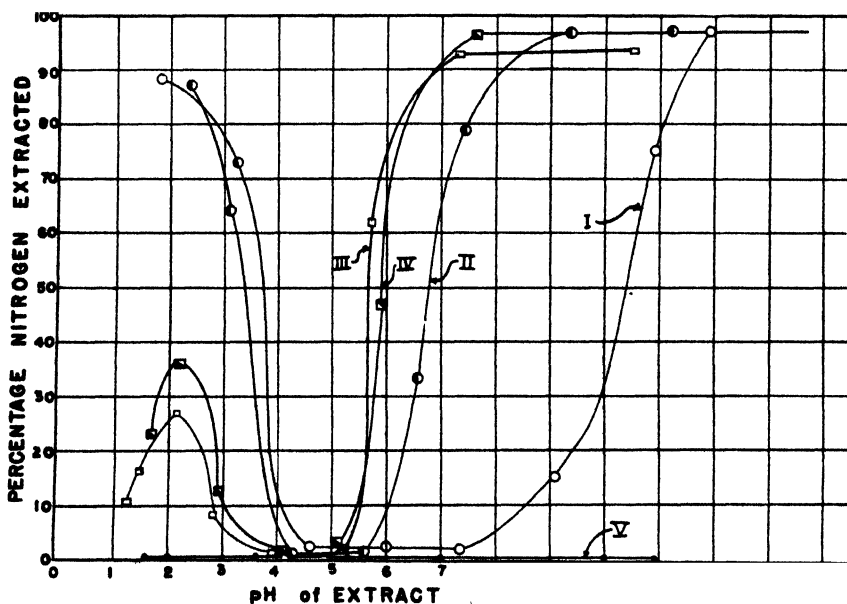


FIG. 2. Effect of formaldehyde on the pH dispersion of rennet and lactic acid caseins. Curves II (rennet) and III (lactic acid), formaldehyde added after pH dispersion; curve V (rennet and lactic acid), formaldehyde added before pH dispersion; curves I (rennet) and IV (lactic acid), no formaldehyde.

pH values. For convenience a single curve, No. V, has been used to represent the dispersion of both caseins by method A. There is, in fact, a small difference in the results for the two caseins, which is not observed in the single curve; the average nitrogen dispersion for the rennet casein is 0.5 per cent and that for the acid casein is 1 per cent higher.

The results for the zein are given in figure 3. The points on the curve above pH 11.0, which are enclosed with broken circles, were not determined with as high an order of precision as the other points. It is observed that the data for zein are different from those for the other proteins, in that there is practically no dispersion by the acid. Curve I represents

the amount of zein dispersed with pH variation but without formaldehyde, and curve II is the dispersion according to procedure B. The relative positions of these two curves are the same as those obtained for the soy-bean proteins and casein under similar treatment.

When zein is dispersed according to procedure A (curve II, figure 3) there is practically no dispersion between pH 1.0 and pH 10.5, but there is a sharp rise in the curve at this latter point. No attempt was made to compare data above pH 10.5 for the various proteins, because the formaldehyde acts as a strong buffer in the region above this point, and the

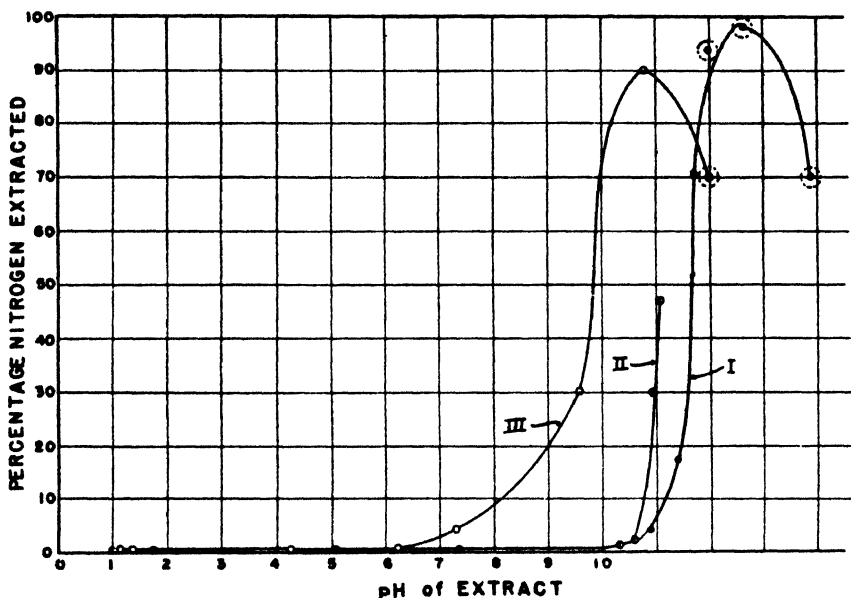


FIG. 3. Effect of formaldehyde on the pH dispersion of zein. Curve III, formaldehyde added after pH dispersion; curve II, formaldehyde added before pH dispersion; curve I, no formaldehyde.

excessive amounts of caustic required to raise the pH would quite probably change the character of the system.

DISCUSSION

Examination of the data shows that the two methods of adding formaldehyde to the protein result in opposite trends with respect to the amount of protein dispersed, that is, when the formaldehyde is added to the protein before the acid or base, the product remains practically undispersed, but when the formaldehyde is added after the dispersing agent, it has the effect of increasing the amount of protein in dispersion on the alkaline side of the isoelectric point or of displacing the curve towards

lower pH values. If the formaldehyde and acid (or base) are mixed together and added to the protein at the same time, a result is obtained that is intermediate between those for methods A and B. Dispersion was accomplished by this procedure, but the results are not reported here.

The first of the above reactions (procedure A) appears to correspond to the well-known hardening action of formaldehyde on protein and is usually attributed to the combination of formaldehyde with the amino groups, which results in lower water absorption. The difference in the results for the second case (procedure B) might be caused by the physical condition of the protein at the time of formaldehyde addition; that is, if the protein is dispersed or partly dispersed at the time of formaldehyde addition, then the protein-formaldehyde reaction might proceed without causing precipitation and the system will be one of reacted protein in the colloidal state. The displacement of the dispersion curve to a lower pH value is also consistent with the above explanation, as the neutralization of the amino groups should tend to decrease the amphoteric properties of the protein, making it relatively a stronger acid and lessening the positive charge on the micelle.

Protein-formaldehyde reaction

The amount of formaldehyde reacting with Hammersten casein, commercial soybean protein, and zein between pH 4.1 and 5.0 as a function of time is given in table 4 and figure 4. The experimental procedure for these measurements was to mix 5 g. of the protein, which had been ground to pass a 100-mesh screen, with 20 ml. of 2 per cent formaldehyde in a tightly stoppered bottle and allow the reaction to proceed with frequent shaking for the period of time indicated in the table. The supernatant solution was filtered from the protein, and the formaldehyde determined by the Romijn method (9). After correcting for a blank the amount of formaldehyde reacting was calculated as the difference between its original and final concentration. Under similar experimental conditions, except for the absence of protein, all of the formaldehyde could be recovered.

The quantity of amino groups in terms of millimoles for 5-g. quantities of the various proteins as determined by the Van Slyke procedure is also given in table 4, and for comparative purposes they are placed on their respective curves at points *a*, *b*, and *c* in figure 4.

The above data show that under the conditions of these experiments the proteins consume substantially more formaldehyde than can be accounted for on the basis of a mole-for-mole reaction between the amino groups and formaldehyde, but, on the other hand, it is less than a one-to-two ratio for these groups for the 48-hr. period shown. An excess of formaldehyde over an amount equivalent to the amino groups would be expected by

this procedure, since the method measures both the chemically reacted and the adsorbed formaldehyde, and therefore it seemed desirable to attempt a separation of the two types of reaction.

TABLE 4
Millimoles of formaldehyde reacting with 5 g. of protein

PROTEIN	MILLIMOLES OF FORMALDEHYDE REACTING WITH 5 G. OF PROTEIN DURING						THEORETICAL*	pH	
	0.5 hr.	1.5 hr.	2.5 hr.	6.0 hr.	24 hr.	48 hr.		Initial	After 24 hr.
Commercial alpha soybean	1.73	2.48	2.58	3.20	3.65	4.03	2.4	4.3	4.1
Hammersten casein	2.12	2.25	2.86	4.02	4.50	4.98	3.2	4.3	4.1
Zein			0.80		0.93	1.24	0	4.5	4.5

* Values for the amino groups on the Hammersten casein and zein were taken from the work of Rutherford, Harris, and Smith (7); the value for the soybean protein was determined in our laboratory by means of a Van Slyke apparatus.

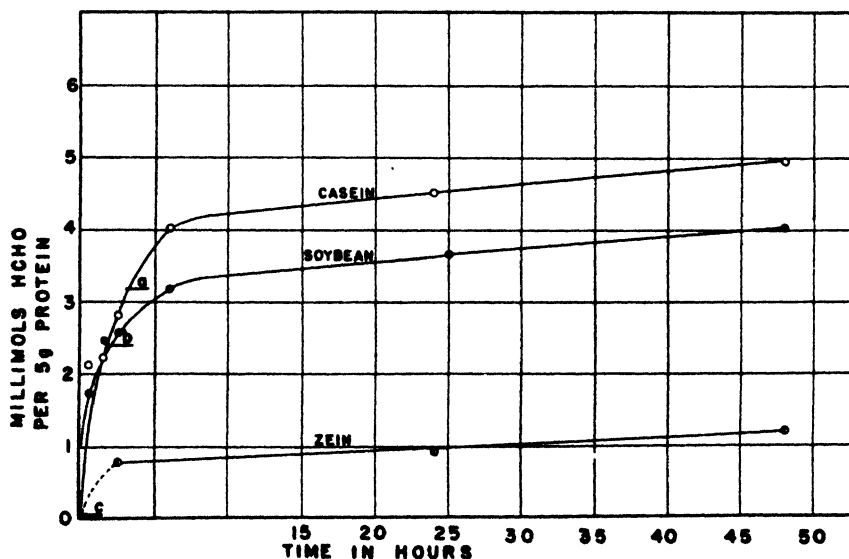


FIG. 4. Curves showing amount of formaldehyde reacting with Hammersten's casein, commercial alpha soybean protein, and commercial zein in relation to time. Points a, b, and c represent amino groups equivalent to 5 g. of protein as determined by Van Slyke's procedure.

The procedure was to treat 200 g. of commercial soybean protein with an excess of formaldehyde for 40 hr., filter, and wash out the excess of unreacted formaldehyde. The washing was a continuous process in which the protein-formaldehyde product was soaked in water for thirty days, during which time the washing was hastened by stirring and changing

the wash water each day. The washings were continued for three days after they gave a negative test (phenylhydrazine-nitroprusside (1)) for formaldehyde.

The amount of formaldehyde remaining in the protein was determined by suspending 2.5 g. of the product in 300 ml. of dilute phosphoric acid (approximately 5 per cent), distilling over 275 ml. of the solution, and analyzing the distillate by the Romijn method for formaldehyde. A correction was made for the method, since it was found by trial that under these conditions only 95 per cent of the formaldehyde is recovered.

The average amount of formaldehyde recovered for three determinations was 0.94 millimole for 2.5 g. of protein, and the correction for the method was 0.06 millimole, making a total value of 1.00 ± 0.03 millimole to compare with a theoretical value of 1.16 ± 0.05 millimoles.

The quantitative relationships between the free amino groups and the amount of formaldehyde reacting is nearer a mole-for-mole reaction than any other simple ratio. However, before the relationship can be definitely substantiated the analytical procedure involved must be improved and the scope of the work enlarged.

SUMMARY

It has been found that proteins may be dispersed in certain aqueous formaldehyde solutions.

A study has been made of the influence of formaldehyde at various hydrogen-ion concentrations on the dispersion of the nitrogenous constituents of soybean oil-free meal, purified soybean protein, commercial alpha protein, self-soured casein, rennet casein, and zein. The different procedures followed were: (A) Formaldehyde was added to the protein, followed by acid or base; (B) the acid or base was added to the protein, followed by the formaldehyde; and (C) acid or base was added without formaldehyde for comparative purposes.

It was found that formaldehyde added by procedure A gave very low nitrogen dispersion between pH values of 1 and 10, but that formaldehyde added by procedure B dispersed as much nitrogen,—and more at some points in the alkaline range,—as when no formaldehyde was present and displaced the curves in the direction of lower pH values.

The effect of concentration of formaldehyde on protein dispersion has also been studied.

The amount of formaldehyde taken up by the various proteins between a pH of 4.1 and a pH of 4.5 during a 24-hr. period has been determined, and the amount of the reacted formaldehyde that cannot be removed by washing with water has been estimated.

REFERENCES

- (1) Association of Official Agricultural Chemists: Methods of Analysis, p. 437 (1935).
- (2) BROTHER, G. H.: Chapter 6 in Sutermeister's Casein and Its Industrial Applications. The Chemical Catalog Co., Inc., New York (1927).
- (3) BENEDICENTI, A.: Arch. Anat. Physiol., Anat. Abt., p. 219 (1897).
- (4) CLARK, G. L., AND ROWAN, R.: Science **87**, 487 (1938).
- (5) GORTNER, R. A.: Chapter 1 in Sutermeister's Casein and Its Industrial Applications. The Chemical Catalog Co., Inc., New York (1927).
- (6) LEVY, M.: J. Biol. Chem. **99**, 767 (1932-33).
TOMYAMA, T.: J. Biol. Chem. **111**, 51 (1935).
WADSWORTH, A., AND PANGBORN, M. C.: J. Biol. Chem. **116**, 423 (1936).
- (7) RUTHERFORD, H. A., HARRIS, MILTON, AND SMITH, A. L.: J. Research Natl. Bur. Standards **19**, 467 (1937).
- (8) SMITH, A. K., CIRCLE, S. J., AND BROTHER, G. H.: J. Am. Chem. Soc. **60**, 1316 (1938).
- (9) TREADWELL AND HALL: Analytical Chemistry, p. 639. John Wiley and Sons, Inc., New York (1935).

THE CONDUCTIVITY OF GELATIN IN ACID SOLUTION¹

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The chemical character of the combination between proteins and acids or bases, emphasized by Procter, Loeb, and others, is now well recognized, a number of workers (2, 5, 8) having pointed out the interrelationships between hydrogen-ion and chloride-ion activity, conductivity, transport number, etc. Prideaux (6) has discussed the conflicting values of the ionic conductance of the gelatin ion per unit charge obtained by a number of methods. Nevertheless, certain discrepancies remain and the present paper presents data (1, 4) on the conductivity and hydrogen-ion activity of gelatin-hydrochloric acid solutions, which it is hoped may yield additional information on certain phases of the problem.

One per cent gelatin solutions containing varying known amounts of acid were made up and their hydrogen-ion activity and conductivity measured. Simultaneously, the conductivity of a solution of the pure acid of the same pH was determined. The procedure is given in more detail below.

EXPERIMENTAL

Eastman Kodak isoelectric gelatin in the form of a 30 per cent gel was electrodialed under 230 volts d.c. in a U-tube. The water in each side arm above the gel was frequently changed, and finally all except the middle third of the gelatin gel was discarded. This was dissolved in warm water to give a 2 per cent solution. Portions of this solution were taken, the desired amounts of acid (standardized against acid potassium phthalate) added, and the solution diluted to 1 per cent gelatin concentration.

Hydrogen-ion activity was determined with the standard hydrogen-platinum electrode, using a saturated calomel half-cell. Conductivities were measured with a Wheatstone bridge with calibrated resistances and vacuum tube amplifier, the cell being standardized with 0.1 *N* potassium chloride. All measurements were made in a thermostat at 25°C.

¹ Presented at the Fifteenth Colloid Symposium, held at Cambridge, Massachusetts, June 9-11, 1938.

RESULTS AND DISCUSSION

The experimentally determined conductivities, with that of the conductivity water subtracted, and the corresponding pH values obtained from the potentiometer readings were plotted against the amount of acid added, and, as a basis for computation, the values of columns 1, 3, and 5 read off these curves. Similar curves for pure hydrochloric acid gave the conductivity values of column 4 as a function of pH.

Columns 6 to 10 are calculated from these data. In a situation such as this, where the exact nature of the phenomena is not well understood,

TABLE 1
Conductivities of gelatin-hydrochloric acid solutions

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
pH	HYDRO- GEN-ION CONCEN- TRATION	ACID ADDED TO GELATIN SOLUTION	SPECIFIC CONDUCT- IVITY OF HYDRO- CHLORIC ACID	SPECIFIC CONDUCT- IVITY OF GELATIN + ACID	SPECIFIC CONDUCT- IVITY OF HYDRO- CHLORIC ACID (COR- RECTED)	SPECIFIC CONDUCT- IVITY OF GELATIN CHLORIDE	GELATIN CHLORIDE	EQUIV- ALENT CONDUCT- IVITY OF GELATIN CHLORIDE	IONIC CONDUCT- TANCE OF GELATIN PER EQUIV- ALENT OF COMBINED CHLORIDE
	<i>equivalents per liter × 10⁴</i>	<i>equivalents per liter × 10⁴</i>	<i>reciprocal ohms × 10⁴</i>	<i>reciprocal ohms × 10⁴</i>	<i>reciprocal ohms × 10⁴</i>	<i>reciprocal ohms × 10⁴</i>	<i>equivalents per liter × 10⁴</i>		
4.86	0.138			0.083					
4.6	0.251	7.0	0.101	0.577	0.093	0.484	6.75	71.6	1.5
4.4	0.398	14.5	0.180	1.217	0.166	1.051	14.10	74.5	4.4
4.2	0.63	24.5	0.301	2.03	0.280	1.75	23.87	73.2	3.1
4.0	1.00	37.5	0.470	3.08	0.432	2.65	36.5	72.7	2.6
3.8	1.58	49.5	0.750	4.26	0.690	3.57	47.9	74.7	4.6
3.6	2.51	58.3	1.17	5.66	1.075	4.585	55.8	82.1	12.0
3.4	3.98	67.0	1.80	7.06	1.655	5.405	63.0	86.0	15.9
3.2	6.30	76.0	2.80	8.56	2.575	5.99	69.7	86.0	15.9
3.0	10.00	84.0	4.45	10.16	4.09	6.07	74.0	82.1	12.0
2.8	15.80	95.0	6.80	12.46	6.25	6.21	79.2	78.5	8.4
2.6	25.10	108.0	10.55	15.96	9.71	6.25	82.9	75.4	5.1
2.4	39.8	125.0	16.95	20.96	15.59	5.37	85.2	63.2	-6.9

any method of calculation is open to question. In table 1 the following technique has been employed: It is well recognized that the conductivities of electrolytes apparently unreactive to gelatin are somewhat reduced by its presence in the solution. For the gelatin employed the magnitude of the reduction was measured with 0.003 and 0.001 *N* potassium chloride solutions and found to average 8 per cent. The assumption was made that the mobilities of hydrogen and chloride ions in the solutions of table 1 were reduced below those for dilute aqueous solutions in the same proportion, i.e., column 6 is 92 per cent of column 4. From the measured conductivity of each gelatin-hydrochloric acid solution (column 5) was sub-

tracted the value of column 6, thus correcting for the conductivity of the free hydrochloric acid in it, the result being the specific conductivity of the gelatin chloride. From column 3, which is the total concentration of the chloride constituent, was subtracted column 2, leaving the chlorine combined with the gelatin in equivalents per liter, whether ionized or not.² Since at 25°C. the ionic conductance of the chloride ion in water is 76.3, in 1 per cent gelatin, with the assumption made above, it should be 70.1. This quantity has been subtracted from the values of column 9. The results, entered in column 10, therefore represent the ionic conductance of the gelatin ion, expressed per equivalent of total chlorine constituent combined with it.

One must first emphasize the point that this final column is obtained by relatively small differences between large quantities, and for this reason alone is liable to considerable error. This is accentuated by the uncertainty as to the depressive action of the gelatin solution on the mobility of the ions, particularly the hydrogen ion. However, after due allowance for these uncertainties, the values of column 10 start initially at very low levels but increase with increasing acid concentration to a maximum at a pH of approximately 3.3, beyond which they fall sharply. While the rise of cataphoretic velocity of the gelatin with increasing acidity is well recognized, the increase in ionic conductance of the gelatin which should correspond thereto has not hitherto been observed. Furthermore, the cataphoretic data (7) indicate a continued rise in gelatin conductance at pH values well below 3, with no sign of a maximum. Thus, Prideaux (6) at pH 3 obtained a value of 25.5 from a plot of cataphoretic velocities against pH. Using the same plot and this method of computation one obtains 18.3 at pH 3.3, where the data here presented indicate a maximum value of 15.9. This discrepancy between the maximum in the conductivity data and the cataphoretic behavior remains unexplained, although the drop in ionic conductance beyond the maximum can be qualitatively accounted for by some factor such as incomplete ionization of the gelatin chloride or increased frictional resistance of the gelatin particle. Below the maximum the rough proportionality of ionic con-

² Electrometric measurement of the chloride-ion concentration (3), while open to some question, indicates that the gelatin chloride begins to be incompletely ionized at a pH of about 3.4. Because of the uncertainties of pCl determination, it seemed wiser here to base computation on the dependable values of chlorine constituent. While hydrogen-ion concentration must be measured and the value used in computation, even a considerable percentage error in it will introduce only a relatively small error in the computation of total chlorine combined with gelatin at low acid concentrations. This technique neglects undissociated hydrochloric acid. Data have been obtained on various organic acids, but interpretation is rendered difficult, e.g., by the presence of considerable undissociated acid.

ductance to charge would indicate a constancy of friction in that range that renders a great increase beyond the maximum unlikely.

At low acid concentrations the gelatin particle carries but little current because of its large particle size, great friction, and small charge upon it. As acid concentration is increased, the charge on the gelatin particle rises rapidly, increasing its tendency to move. However, its particle size probably changes but little, so that the frictional resistance to motion remains relatively constant, thus accounting for the increased mobility per unit of combined chlorine. Finally, nonionization begins to play a part and ionic conductance per unit of combined chlorine falls off.

REFERENCES

- (1) COYNE: The Conductivity of Gelatin Solutions. Chemical Engineering Thesis, Massachusetts Institute of Technology, 1931.
- (2) FERGUSON AND BACON: J. Am. Chem. Soc. **49**, 1921 (1927).
- (3) HITCHCOCK: J. Gen. Physiol. **5**, 383 (1922-23).
- (4) MOSS AND SMITH: The Conductivity of Gelatin Solutions. Chemical Engineering Thesis, Massachusetts Institute of Technology, 1931.
- (5) PAULI AND VALKÓ: Kolloidchemie der Eiweisskörper, Part VI, Handbuch der Kolloidwissenschaft. Theodor Steinkopff, Dresden (1933).
- (6) PRIDEAUX: Trans. Faraday Soc. **31**, 349 (1935).
- (7) PRIDEAUX AND HOWITT: Proc. Roy. Soc. (London) **A126**, 126 (1929).
- (8) SCHUKAREV AND VDOVENKO: Physik. Z. Sowjetunion **4**, 894 (1933).

AN INVESTIGATION OF CERTAIN PROPERTIES OF HYDROUS LANTHANUM HYDROXIDE SOLS¹

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INTRODUCTION

Hydrous lanthanum hydroxide sols have been prepared by several investigators. The methods used have included dialysis after the addition of small amounts of ammonia to lanthanum acetate solutions (6, 1), electrolysis of a lanthanum chloride solution using a mercury cathode (14), peptization of the freshly precipitated and well-washed hydroxide with dilute hydrochloric acid (2, 9), addition of less than 2.6 equivalents of sodium hydroxide to solutions of lanthanum nitrate or chloride (3, 17), and the "peptization" of lanthanum hydroxide with sucrose or levulose (18).

Inasmuch as detailed studies on colloidal lanthanum hydroxide have been limited to x-ray proof of the crystallinity of the sol particles (2), some viscosity measurements (9), and recognition of the colloidal nature of the color reaction between lanthanum hydroxide and iodine in the presence of acetate (5, 1, 13, 12), it was felt that an examination of a few characteristics of these sols would be of value.

PREPARATION AND PURIFICATION OF SOLS

Of the preparative methods previously reported, peptization of a boiling suspension of lanthanum hydroxide with dilute hydrochloric acid is the most satisfactory. However, this method necessitates the use of freshly precipitated hydroxide, and the comparatively long time required for the production of even moderately concentrated sols brings about aging effects which render the precipitate very resistant to the action of the peptizing agent.

A method eliminating these difficulties has been described (16). Data for some of the sols prepared by this procedure and dialyzed with carbon dioxide-free water (16) are given in table 1. In each instance the purity ratio is to be taken as the ratio of the equivalents of lanthanum oxide present to the equivalent of chloride.

¹ This paper is a portion of a thesis submitted by Therald Moeller to the Faculty of the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1938.

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ABSORPTION OF CARBON DIOXIDE

The impossibility of purifying hydrous lanthanum hydroxide sols by dialysis with water containing dissolved carbon dioxide and the necessity of protecting sols from the air have been discussed (16).

Since lanthanum carbonate is insoluble and settles out when it forms, the absorption of carbon dioxide by a sol exposed to the air can be followed by periodic analyses for the lanthanum hydroxide remaining in suspension. Observations upon two portions of sol 6f, one exposed to the air and the other protected by a paraffin seal, showed that the protected sol

TABLE 1
Data for lanthanum hydroxide sols

SOL	NH ₄ OH PER CENT OF EQUIVALENT	TIME DIALYZED*	La ₂ O ₃	Cl ⁻	PURITY RATIO	pH
		hours	grams per liter	grams per liter		
6c.....	33.3	40	0.250	0.023	3.6	6.9
6d.....	33.3	45	0.500	0.017	9.6	7.0
6e.....	33.3	48	0.829	0.034	8.0	7.4
6f.....	33.3	51	0.755	0.037	6.7	
6g.....		84	0.438	0.011	13.0	7.3
6h(1).....	50.0	67	1.158	0.103	3.7	7.8
6h(2).....	67.0	67	1.984	0.061	10.6	8.3
6h(3).....	89.0	67	2.312	0.049	15.4	7.9
6i.....	50.0	85	0.736	0.015	16.0	6.6
6j.....	60.0	80	2.121	0.056	12.4	
6k†.....			0.766	0.006	41.8	
6l†.....			0.732	0.024	10.0	
6m.....	80.0	80	1.406	0.031	28.7	
6n†.....			1.492	0.031	15.7	
6x.....	87.5	41	4.04	0.058	22.8	
6y.....	87.5	41	3.99	0.061	21.4	
6z.....	33.33	120	0.553	0.015	12.1	

* All sols dialyzed at 20–25°C. except 6i, 6j, 6m, 6x, and 6y, which were dialyzed at 35–40°C.

† These sols were residues from other sols.

remained unchanged in concentration for sixteen weeks, whereas the unprotected sol began to deposit lanthanum carbonate after two weeks and was completely destroyed after twenty-four weeks.

THE STABILITY OF LANTHANUM HYDROXIDE SOLS AS MEASURED BY
FLOCCULATION VALUES

A. Experimental technique

Flocculation values were determined as follows: Into carefully cleaned Pyrex test tubes varying amounts of the electrolyte solutions were meas-

ured by means of a microburet. Sufficient carbon dioxide-free distilled water to make a total volume of 5 ml. was added to each from another microburet, followed by 5 ml. of the sol. Each tube was shaken vigorously and stoppered. Observations were made after 2 hr.

The flocculation value for a given electrolyte was then obtained from that concentration of electrolyte midway between the least amount necessary for complete flocculation and the next smaller amount. The results have all been calculated as millimoles of electrolyte per liter of combined sol and electrolyte solution, and are to be interpreted as the liminal concentrations which just cause complete coagulation after 2 hr. The values were easily reproducible in all cases.

In order to minimize the effects of carbon dioxide, carbon dioxide-free water was used for all solutions, and the sols were placed in flasks from which they could be transferred to 5-ml. burets in an atmosphere of carbon dioxide-free air.

Most of the electrolytes used were of Merck reagent or Mallinckrodt analytical reagent grade. A few were c.p. salts and were purified by repeated recrystallization from doubly distilled water. Calibrated flasks and weights were used throughout.

B. Effect of sol purity

From the method of preparation, it seems likely that lanthanum hydroxide sols are stabilized by lanthanum chloride, or more particularly by lanthanum ion. If this be true, then the stability of a sol should be a function of the amount of lanthanum chloride present. Furthermore, the flocculation values should, in general, increase as the purity ratio decreases, assuming equal sol concentrations, for the smaller the purity ratio, the larger the amount of stabilizing electrolyte present. Both of these statements have been verified.

Interesting results upon the effect of sol purity were obtained during an attempt to investigate the influence of pH upon sol stability. Since Hazel and Sorum (10) had shown that the stability of ferric oxide sols is increased by increasing the hydrogen-ion concentration with hydrochloric acid, it was thought that hydrous lanthanum hydroxide sols might show the same behavior. Accordingly, samples of sol 6e were diluted as shown in table 2, the pH being determined on each portion with a glass electrode.

Flocculation values determined upon these portions are summarized in table 3. Except with lanthanum chloride, monobasic potassium phosphate, and potassium ferrocyanide, there is a general increase in flocculation value with decrease in pH. This increase is quite steady until portion 5 is reached, but between portions 4 and 5 and 5 and 6 a sudden and very marked increase in stability occurs in a pH range of only 0.33. It seems odd for a sol of this type that such a pronounced change in stability should occur in such a small pH interval, especially since between por-

tions 1 and 2, where the pH change is a trifle greater, only slight changes in stability are noted. Ferric oxide sols show no such tendencies.

The slight pH changes and the highly basic nature of lanthanum hydroxide suggested that the acid which was added had reacted with the colloidal particles, converting them into stabilizing lanthanum chloride.

TABLE 2
Dilution of sol 6e

PORTION	DILUTED WITH	pH
1	Equal volume of water	7.43
2	Equal volume of <i>M</i> /4000 HCl	7.03
3	Equal volume of <i>M</i> /2000 HCl	6.85
4	Equal volume of <i>M</i> /1000 HCl	6.67
5	Equal volume of <i>M</i> /500 HCl	6.56
6	Equal volume of <i>M</i> /250 HCl	6.34

TABLE 3
Flocculation values for sol 6e

PORTION..... pH.....	1 7.43	2 7.03	3 6.85	4 6.67	5 6.56	6 6.34
ELECTROLYTE	FLOCCULATION VALUE, IN MILLIMOLES PER LITER					
LaCl ₃		115	115	120		
KCl.....	8.5	11.5	20	29	49	84
KBr.....		17	22	27	46	76
KI.....			25	32	40	66
KNO ₃	9.5	13	23	25	37	58
LiCl.....		17.5	22.5	27	38	51
KF.....			1.05	1.1	1.55	2.45
Na ₂ SO ₄	0.115	0.155	0.175	0.185	0.215	0.335
K ₂ SO ₄	0.105	0.145	0.165	0.175	0.205	0.325
MgSO ₄	0.105	0.145	0.155	0.165	0.205	0.330
K ₂ CrO ₄	0.045	0.075	0.085	0.095	0.120	0.200
K ₂ Cr ₂ O ₇	0.038	0.043	0.053	0.058	0.068	0.103
KH ₂ PO ₄	0.068	0.128	0.150	0.153	0.143	0.130
K ₂ AsO ₄	0.048	0.088	0.128	0.160	0.430	0.700*
K ₃ PO ₄	0.028	0.063	0.053	0.153	0.270	0.450
K ₄ Fe(CN) ₆	0.007	0.009	0.009	0.010	0.006	0.005

* Does not appear in figure 3.

If this were true, the flocculation values should then bear some relation to the amount of lanthanum chloride formed or to the hydrochloric acid added.

In table 4 are given data relative to the amounts of acid added and the lanthanum chloride produced, assuming exact equivalence. Since the

lanthanum chloride content is increased much more between portions 4 and 6 than between the other portions, a comparatively large increase in stability should occur in this interval.

Data from table 3 are plotted against the calculated lanthanum chloride contents from table 4 in figures 1, 2, and 3. For all electrolytes except

TABLE 4
Impurities in sol 6e

PORTION	FINAL HYDROCHLORIC ACID CONCENTRATION	LANTHANUM CHLORIDE EQUIVA- LENT TO HYDROCHLORIC ACID
	<i>millimoles per liter</i>	<i>millimoles per liter</i>
1	0	0
2	0.125	0.042
3	0.250	0.084
4	0.500	0.167
5	1.000	0.333
6	2.000	0.667

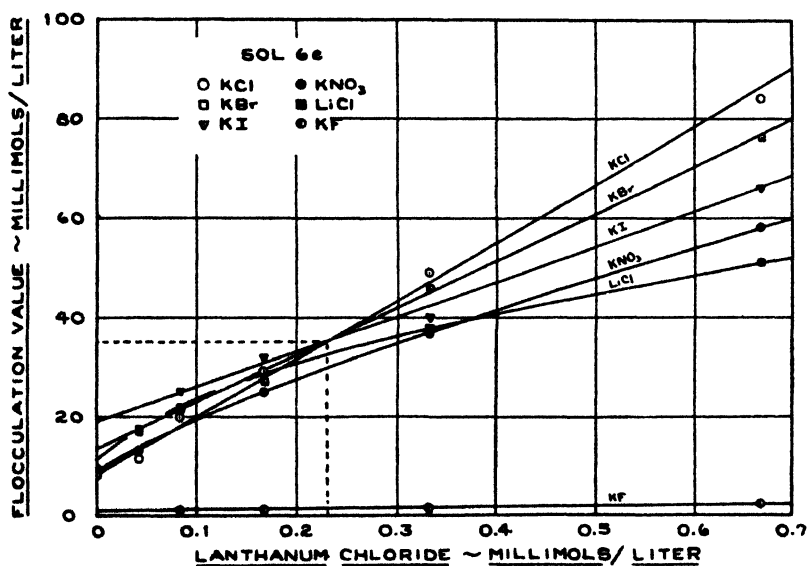


Fig. 1. Effect of sol purity upon stability

monobasic potassium phosphate and potassium ferrocyanide the flocculation values increase smoothly with sol impurity, there being no sudden breaks in the curves, thus supporting the contention that the increased stability upon the addition of hydrochloric acid is due to the formation of lanthanum ion in the sol.

The shape of the curve seems to be somewhat dependent upon the val-

ence of the anion of the flocculating electrolyte. Several other points of interest are to be noted. First, the curves for potassium chloride, potas-

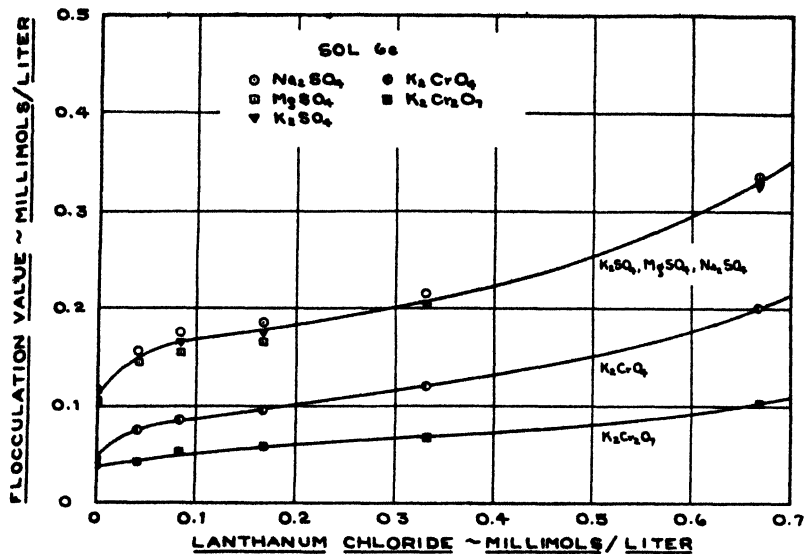


FIG. 2. Effect of sol purity upon stability

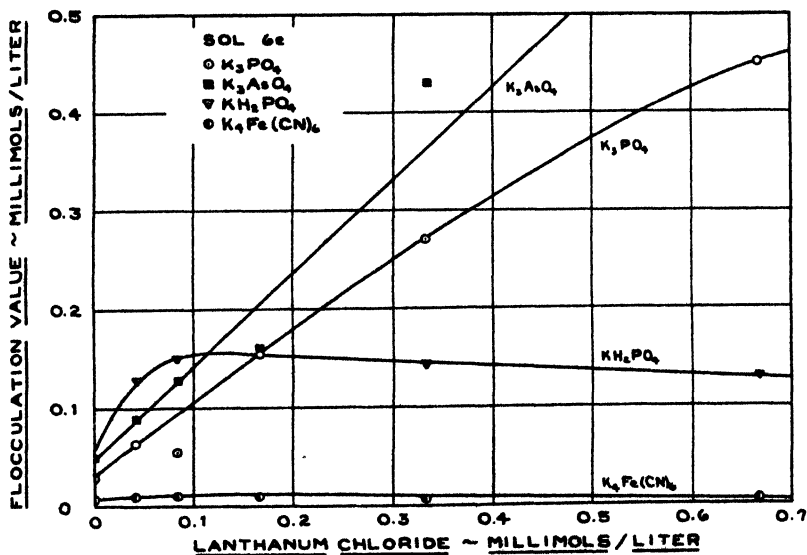
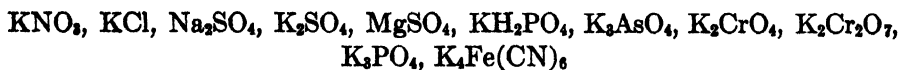


FIG. 3. Effect of sol purity upon stability

sium bromide, and potassium iodide all cross at a common point. At this intersection a reversal in the order of effectiveness of the three halides as flocculating agents occurs. The reason is obscure.

Second, the values for the three sulfates lie along a common curve, indicating that the nature of the cation is of almost negligible importance in flocculating the sols.

Third, the order of relative effectiveness of the salts as flocculating agents seems to be a function of sol purity. Thus the order of decreasing flocculation values for the original is



while for the most impure sol it is

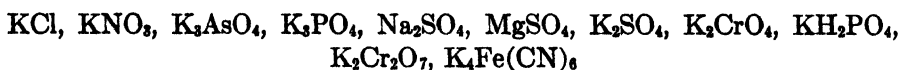


TABLE 5

Effect of lanthanum chloride upon flocculation values for sol 6k

ELECTROLYTE	FLOCCULATION VALUE, IN MILLIMOLES PER LITER		
	Sol 6k(1)	Sol 6k(2)	Sol 6k(3)
KH_2PO_4	0.05	0.170	0.230
K_3AsO_4	0.048	0.140	0.230
K_3PO_4	0.018	0.083	0.145
$\text{K}_4\text{Fe}(\text{CN})_6$	0.013	0.018	0.021
$\text{K}_4\text{Fe}(\text{CN})_6$	0.008	0.012	0.015

Sol 6k(1): No added lanthanum chloride.

Sol 6k(2): 0.11 millimole of lanthanum chloride per liter.

Sol 6k(3): 0.22 millimole of lanthanum chloride per liter.

the most surprising changes being with tribasic potassium phosphate and potassium arsenate.

Fourth, the curves for monobasic potassium phosphate and potassium ferrocyanide show unexplained maxima.

Lanthanum chloride exerts a similar stabilizing effect. Data obtained for sol 6k, which are given in table 5 and figure 4, show a close parallel to those values for hydrochloric acid in equivalent regions. Again the behavior of monobasic potassium phosphate is peculiar.

C. Effect of dilution

Although the application of the Burton-Bishop rule (4) to hydrous oxide and hydroxide sols has been disputed, Sorum and his coworkers (11, 7) have shown that while highly purified ferric oxide and chromic oxide sols follow the rule, treatment with ferric and chromic chlorides, respectively, causes them to require decreasing amounts of all electrolytes for floccula-

tion after dilution. It will be shown that hydrous lanthanum hydroxide sols exhibit the same characteristics.

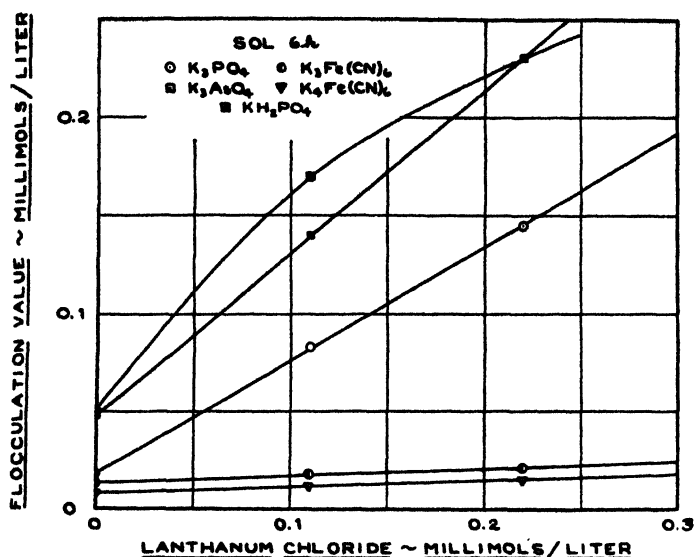


FIG. 4. Effect of sol purity upon stability

TABLE 6

Effect of dilution upon flocculation values of sol 6i

ELECTROLYTE	FLOCCULATION VALUE, IN MILLIMOLS PER LITER				
	100 per cent	80 per cent	60 per cent	40 per cent	20 per cent
1. Monovalent anions:					
KBr.....	14	12	11	10	*
KCl.....	11	10	9	9.5	*
KF.....	0.30	0.35	0.40	0.45	0.60
2. Divalent anions:					
K ₂ SO ₄	0.165	0.165	0.165	0.160	0.170
K ₂ CrO ₄	0.075	0.075	0.075	0.075	0.075
K ₂ Cr ₂ O ₇	0.060	0.060	0.060	0.060	0.060
3. Trivalent anions:					
K ₃ AsO ₄	0.043	0.038	0.032	0.025	0.018
K ₃ PO ₄	0.028	0.023	0.018	0.014	0.008
4. Tetravalent anion:					
K ₄ Fe(CN) ₆	0.006	0.004	0.003	0.004	0.002

* Sol too dilute for accurate observations.

Flocculation values obtained for sol 6i are summarized in table 6, where sol concentrations are expressed as per cent of the original sol

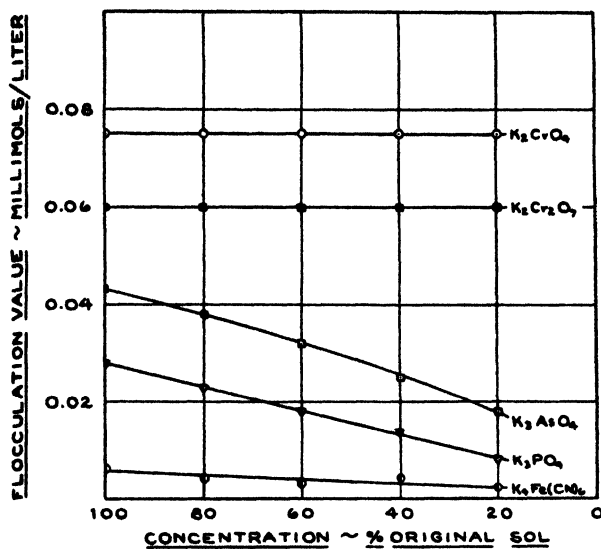


FIG. 5. Effect of dilution upon sol stability

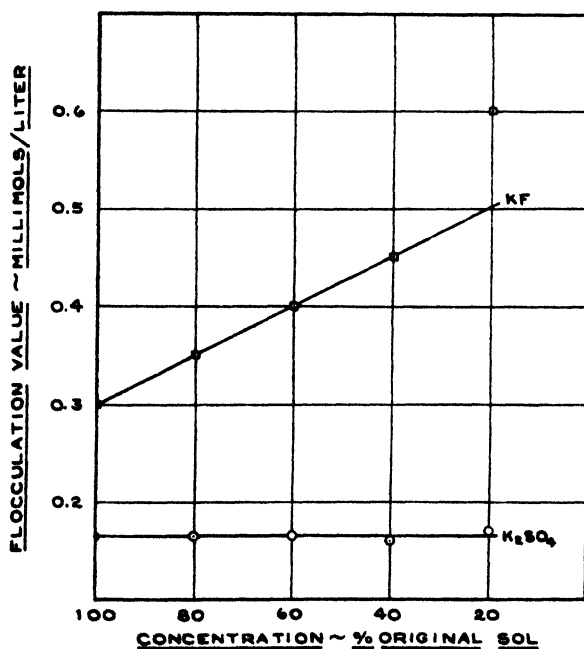


FIG. 6. Effect of dilution upon sol stability

present. Some of these data are plotted in figures 5 and 6. This sol follows the Burton-Bishop rule for all electrolytes investigated except potassium chloride and potassium bromide.

The effects of dilution after the addition of lanthanum chloride are shown in table 7, where the 100 per cent sol received 0.19 millimole of lanthanum chloride per liter and the others proportionally smaller

TABLE 7
Effect of dilution upon sol 6i (treated)

ELECTROLYTE	FLOCCULATION VALUE, IN MILLIMOLES PER LITER		
	100 per cent	40 per cent	20 per cent
1. Monovalent anion:			
KF	0.88	0.65	0.60
2. Divalent anions:			
K ₂ SO ₄	0.30	0.23	0.25
K ₂ CrO ₄	0.155	0.125	0.115
K ₂ Cr ₂ O ₇	0.095	0.070	0.055
3. Tetravalent anion:			
K ₄ Fe(CN) ₆	0.008	0.004	0.002

TABLE 8
Effect of dilution upon flocculation values of sol 6m

ELECTROLYTE	FLOCCULATION VALUE, IN MILLIMOLES PER LITER		
	100 per cent	75 per cent	50 per cent
1. Monovalent anion:			
KBr	2.5	3.5	4.5
2. Divalent anions:			
K ₂ SO ₄	0.075	0.085	0.095
K ₂ Cr ₂ O ₇	0.065	0.065	0.065
3. Trivalent anions:			
K ₃ AsO ₄	0.043	0.043	0.038
K ₃ PO ₄	0.023	0.023	0.023
4. Tetravalent anion:			
K ₄ Fe(CN) ₆	0.006	0.006	0.005

amounts. Decreasing amounts of all electrolytes are required as the sol is diluted.

Further evidence of the application of the Burton-Bishop rule to highly purified sols is given in table 8. Here potassium bromide also followed the rule, but the effects were less noticeable with the anions of higher valence, perhaps because of the greater purity of this sol (see table 1). Data in table 9 show that again the addition of lanthanum chloride caused the sol to exhibit "normal effects" upon dilution. Again the 100 per cent sol was

treated with 0.19 millimole of lanthanum chloride per liter and the others with proportionally less.

D. Effect of alcohol

If the stability of a hydrous oxide or hydroxide sol be due in part to hydration, the addition of a dehydrating agent such as alcohol or acetone

TABLE 9
Effect of dilution upon sol 6m (treated)

ELECTROLYTE	FLOCCULATION VALUE, IN MILLIMOLES PER LITER		
	100 per cent	75 per cent	50 per cent
1. Monovalent anion:			
KBr.	34	29	25
2. Divalent anions:			
K ₂ SO ₄	0.27	0.24	0.21
K ₂ Cr ₂ O ₇	0.115	0.105	0.085
3. Trivalent anions:			
K ₃ AsO ₄	0.243	0.173	0.118
K ₃ PO ₄	0.133	0.103	0.073
4. Tetravalent anion:			
K ₄ Fe(CN) ₆	0.021	0.016	0.011

TABLE 10
Effect of alcohol upon sol 6l

ELECTROLYTE	FLOCCULATION VALUE, IN MILLIMOLES PER LITER	
	Sol 6l(3)	Sol 6l(3)'
KCl.	25	22
KF.	1.15	0.85
K ₂ SO ₄	0.21	0.15
K ₂ CrO ₄	0.13	0.115
K ₂ Cr ₂ O ₇	0.09	0.08
K ₃ AsO ₄	0.175	0.145
K ₃ PO ₄	0.108	0.093
K ₄ Fe(CN) ₆	0.008	0.008

should render that sol more sensitive to flocculation by electrolytes. Reports in the literature are, however, conflicting (19).

In table 10 are summarized some flocculation values obtained with sol 6l. A part of sol 6l was divided into two 750-ml. portions, one of which, 6l(3), was treated with 250 ml. of water, and the other, 6l(3)', with 250 ml. of 95 per cent ethyl alcohol. With the exception of the ferrocyanide all anions, regardless of valence, were more effective in flocculating the sol treated with alcohol. However, the small differences

in flocculation values between the two sols indicate that the dehydrating action was not very pronounced and that, therefore, only a small amount of the stability of lanthanum hydroxide sols can be ascribed to hydration, the major part being due to adsorbed lanthanum ion. Furthermore, neither alcohol nor acetone alone is capable of flocculating these sols, indicating the absence of excessive hydration.

E. Discussion

From the results presented it may be concluded that the stability of lanthanum hydroxide sols is influenced chiefly by purity and sol concentration.

The apparent impossibility of obtaining sols that give exactly the same flocculation values for a given salt is to be expected, for the conditions of dialysis could not be sufficiently accurately controlled to yield sols of constant concentration and purity. Consequently, no attempt has been made to ascribe to lanthanum hydroxide sols in general a definite flocculation value for each electrolyte. Each sol possesses its own stability and can be characterized by the flocculation values obtained for it.

The data for sol 6e have indicated that the lyotropic order depends somewhat upon sol purity. Taking this into account and using only the results for the more nearly pure sols, it has been possible to compile the following series for the potassium salts, in which the anions are arranged in order of increasing flocculation values: ferrocyanide, ferricyanide, tribasic phosphate, arsenate, dichromate, monobasic phosphate, chromate, sulfate, fluoride, nitrate, chloride, bromide, and iodide. The arrangement in this series agrees well with those reported for ferric oxide (10) and beryllium oxide (15) sols. The values for lanthanum hydroxide are of the same magnitude as those for ferric oxide but are much smaller than those for beryllium oxide.

By analogy to other sols, it is probable that the stabilizing lanthanum ion is adsorbed on the suspended particles. Since Böhm and Niclassen (2) have shown that the sol particles give the same x-ray pattern as precipitated lanthanum hydroxide, it is likely that these particles, too, are lanthanum hydroxide.

HYDROUS LANTHANUM HYDROXIDE SOLS AND THE IRREGULAR SERIES

Flocculation studies with tribasic potassium phosphate indicated that lanthanum hydroxide sols containing considerable phosphate flocculate much more slowly than those containing smaller quantities of the electrolyte. Such observations suggested an irregular series, and it was found that lanthanum hydroxide sols are recharged by tribasic potassium phosphate.

A series of experiments was carried out with sol 6k. This sol was di-

vided into three portions, which were treated as indicated in table 5. Five-milliliter samples of these sols were observed in the presence of increasing concentrations of several electrolytes yielding polyvalent anions, according to the method used for the determination of flocculation values. The results are given in table 11. Of the electrolytes investigated, only the tribasic phosphate gave an irregular series. In no other instance was there any evidence of a recharging effect. For the tribasic phosphate,

TABLE 11
The irregular series for sol 6k

ELECTROLYTE	CONCENTRATION IN MILLIMOLES PER LITER	OBSERVATIONS (2 HR.)	ELECTRO- PHORETIC MIGRATION
A. Sol 6k(1)			
1. K_3PO_4	0 to 0.018	No coagulation	To cathode
	0.018 to 0.215	Complete coagulation	
	0.215 to 95	No coagulation	To anode
	95 up	Complete coagulation	
2. KH_2PO_4	0 to 0.05	No coagulation	To cathode
	0.05 to 50	Complete coagulation	
3. K_3AsO_4	0 to 0.048	No coagulation	To cathode
	0.048 to 50	Complete coagulation	
4. $K_3Fe(CN)_6$	0 to 0.013	No coagulation	To cathode
	0.013 to 50	Complete coagulation	
5. $K_4Fe(CN)_6$	0 to 0.008	No coagulation	To cathode
	0.008 to 50	Complete coagulation	
B. Sol 6k(2)			
1. K_3PO_4	0 to 0.083	No coagulation	To cathode
	0.083 to 0.75	Complete coagulation	
	0.75 to 37	No coagulation	To anode
	37 up	Complete coagulation	
2. KH_2PO_4	0 to 0.170	No coagulation	To cathode
	0.170 to 50	Complete coagulation	
3. K_3AsO_4	0 to 0.140	No coagulation	To cathode
	0.140 to 50	Complete coagulation	
4. $K_3Fe(CN)_6$	0 to 0.018	No coagulation	To cathode
	0.018 to 50	Complete coagulation	
5. $K_4Fe(CN)_6$	0 to 0.012	No coagulation	To cathode
	0.012 to 50	Complete coagulation	

TABLE 11—*Continued*
The irregular series for sol 6k
 C. Sol 6k(3)

1. K_3PO_4	0 to 0.145 0.145 to 1.0 1.0 to 31 31 up	No coagulation Complete coagulation No coagulation Complete coagulation	To cathode To anode
2. KH_2PO_4	0 to 0.230 0.230 to 50	No coagulation Complete coagulation	To cathode
3. K_3AsO_4	0 to 0.230 0.230 to 50	No coagulation Complete coagulation	To cathode
4. $K_3Fe(CN)_6$	0 to 0.021 0.021 to 50	No coagulation Complete coagulation	To cathode
5. $K_4Fe(CN)_6$	0 to 0.015 0.015 to 50	No coagulation Complete coagulation	To cathode

the narrowed stability range for the negative sol with increasing lanthanum chloride concentrations is to be expected, for the lanthanum ion will add its zeta potential-raising power to that of the potassium ion and thereby promote flocculation of the negative sol at lower potassium phosphate concentrations.

Observations upon another sol indicated that dibasic potassium phosphate gave evidences of a slight recharging effect. Thus for lanthanum hydroxide sols it appears that the tribasic phosphate ion is specific in producing the irregular series, and in the series tribasic phosphate, dibasic phosphate, monobasic phosphate the recharging effects decrease with decreasing concentrations of PO_4^{---} ion.

Negative lanthanum hydroxide sols, while resembling the positive sols in appearance, are much less stable and flocculate after 24 to 36 hr.

DENSITY MEASUREMENTS

With regard to the density of a hydrophobic sol, Freundlich (8) states that it "may be represented by a linear equation" dependent upon sol concentration. Results of density determinations upon sols 6x and 6y are given in table 12 and figure 7. The original sols were diluted to the desired concentrations with carbon dioxide-free distilled water, and the values were obtained with a calibrated 10-ml. pycnometer at $25^\circ C. \pm 0.01^\circ$. All data are referred to $4^\circ C$. Thus the densities of hydrous lanthanum hydroxide sols vary linearly with the amount of the dispersed material.

MISCELLANEOUS

Hydrous lanthanum hydroxide sols exhibit a well-defined Tyndall effect, and the particles may be distinguished as points of light with the ultramicroscope.

TABLE 12
Density measurements

Sol 6x		Sol 6y	
La_2O_3	DENSITY	La_2O_3	DENSITY
grams per liter	grams per cc.	grams per liter	grams per cc.
4.04	1.0005	3.99	1.0003
3.64	1.0002	3.59	1.0000
3.23	0.9998	3.19	0.9995
2.83	0.9994	2.79	0.9991
2.42	0.9991	2.39	0.9989
2.02	0.9988	2.00	0.9987
1.62	0.9984	1.60	0.9985
1.21	0.9981	1.20	0.9980
0.81	0.9977	0.80	0.9977
0.40	0.9973	0.40	0.9972
0	0.9970	0	0.9970

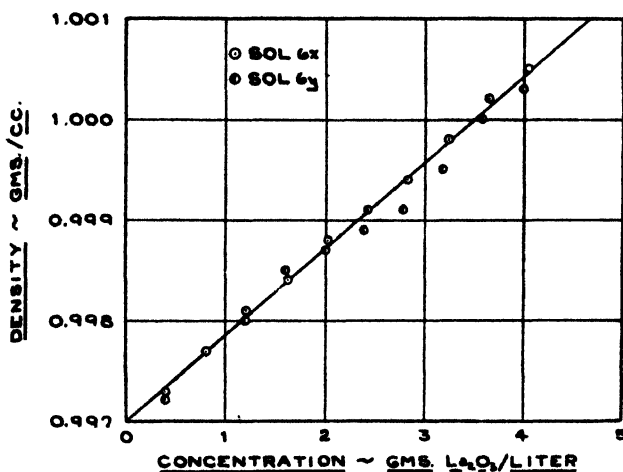


FIG. 7. Density of sols

Undialyzed sols may be boiled or frozen without flocculation. Dialyzed sols, however, are readily coagulated by boiling or freezing. The coagulum from a boiled sol is crystalline and finely divided, indicating the aging effects of heating.

SUMMARY

1. Stable lanthanum hydroxide sols have been prepared and purified by dialysis.
2. All sols absorb carbon dioxide from the air. The reduction in sol concentration due to carbonate formation has been followed.
3. The stability of the dialyzed sols, as measured by flocculation values, has been investigated under a variety of conditions. The addition of lanthanum chloride or hydrochloric acid stabilizes the sols. Very pure sols follow the Burton-Bishop rule, but the addition of small amounts of lanthanum chloride causes these sols to exhibit "normal" effects upon dilution. Alcohol exerts a sensitizing effect.
4. A lyotropic series has been set up.
5. An irregular series has been found for tribasic potassium phosphate, but not for similar electrolytes. The addition of lanthanum chloride narrows the region of stability of the negative sol.
6. The densities of lanthanum hydroxide sols vary linearly with sol concentration.
7. A few qualitative observations have been given.

REFERENCES

- (1) BILTZ: Ber. **37**, 719 (1904).
- (2) BÖHM AND NICLASSEN: Z. anorg. Chem. **132**, 1 (1923).
- (3) BRITTON: J. Chem. Soc. **127**, 2142 (1925).
- (4) BURTON AND BISHOP: J. Phys. Chem. **24**, 701 (1920).
- (5) DAMOUR: Compt. rend. **43**, 976 (1856).
- (6) DELAFONTAINE: Chem. News **73**, 284 (1896).
- (7) FISHER AND SORUM: J. Phys. Chem. **39**, 283 (1935).
- (8) FREUNDLICH: Colloid and Capillary Chemistry, p. 365. E. P. Dutton and Co., New York (1926).
- (9) FREUNDLICH AND SCHALEK: Z. physik. Chem. **108**, 153 (1924).
- (10) HAZEL AND SORUM: J. Am. Chem. Soc. **53**, 49 (1931).
- (11) JUDD AND SORUM: J. Am. Chem. Soc. **52**, 2598 (1930).
- (12) KRÜGER AND TSCHIRCH: Ber. **62B**, 2776 (1929).
- (13) LOTTERMOSER: Kolloid-Z. **33**, 271 (1923).
- (14) MCCUTCHEON AND SMITH: J. Am. Chem. Soc. **29**, 1460 (1907).
- (15) MADSON AND KRAUSKOPF: J. Phys. Chem. **35**, 3237 (1931).
- (16) MOELLER AND KRAUSKOPF: J. Am. Chem. Soc. **60**, 726 (1938).
- (17) SADOLIN: Z. anorg. Chem. **160**, 133 (1927).
- (18) SEN: Z. anorg. allgem. Chem. **174**, 61 (1928).
- (19) THOMAS: Colloid Chemistry, p. 195. McGraw-Hill Book Co., New York (1934).

THE ANOMALOUS EFFECT OF MAGNESIUM CHLORIDE UPON THE DISSOCIATION OF WEAK ACIDS

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In two papers published in this Journal Simms (4) called attention to the anomalous effect of the magnesium ion upon the dissociation of weak acids. Since the author of this paper has, in the course of other work (2), come to the conclusion that the calcium salts of organic acids, and of sulfuric and phosphoric acids as well, are only partly dissociated, it seemed possible that the anomalous effects obtained by Simms might similarly be due to incomplete dissociation of the magnesium salts.

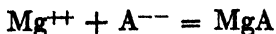
The discussion in this paper will be limited to four of the acids with which Simms observed the greatest effects, *viz*, oxalic, malonic, aspartic, and aminoacetic acids.¹

From the equation

$$\text{pH} = \text{pK} + \log \frac{\text{anion}}{\text{acid}}$$

It is evident that the addition of Mg^{++} , or of any other cation capable of forming a complex with the anion, must decrease the pH of the solution. To bring the solution back to its original pH will require a certain amount of base. At this pH the acid not bound as complex will, of course, be distributed as free acid, as monanion and as dianion, in exactly the same proportions as in a solution containing the same amount of total acid but no Mg^{++} or other cation capable of forming a complex with either of the anions.

At any given pH, let b' = corrected equivalents of base per mole of acid in the absence of Mg^{++} , and B' = corrected equivalents of base per mole of total acid in the presence of Mg^{++} . If we assume that the reaction in the case of dibasic acids is



then

$$B' = b'(1 - \text{MgA}) + 2\text{MgA}$$

¹ The case of citric acid will be considered by Cannan and Abels in another communication.

from which

$$\text{MgA} = \frac{B' - b'}{2 - b'} \quad (1)$$

The data of Simms for pH, B' , and b' were plotted on large-scale co-ordinate paper. There were thus obtained, for each acid, two pairs of curves, one for solutions of $\sqrt{\mu} \cong 0.20$ and the other for solutions of $\sqrt{\mu} \cong 0.28$. From each of these, three points were taken, representing the two extreme observed points at which direct comparisons were possible and one intermediate one.

The treatment of one pair of figures for oxalic acid will be given in detail. In a solution containing a total of 9.53 millimoles of oxalate and 25 millimoles of magnesium chloride at pH = 2.885, $b' = 1.102$ and $B' = 1.510$. From equation 1,

$$[\text{MgOx}] = \frac{B' - b'}{2 - b'} 9.53 = 4.33 \text{ millimoles}$$

The removal of this much Mg^{++} and of the same amount of oxalic acid (in its three forms) lowered $\sqrt{\mu}$ from 0.292 to 0.266. At this ionic strength,

$$b'_1 = \frac{H^+K_1 + 2K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2}$$

Using values for K_1 and K_2 given by Simms (4, 5),

$$b'_1 = 1.078$$

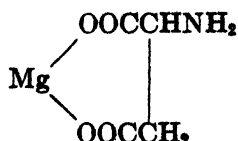
We now obtained $\text{MgOx} = 4.46$ millimoles, from which the remaining oxalic acid = 5.07 millimoles and $\text{Mg}^{++} = 20.54$ millimoles. $\sqrt{\mu}$ was now 0.265. The concentration of Ox^{--} was then calculated to be 0.460, and the value of K to be

$$K = \frac{[\text{Mg}^{++}][\text{Ox}^{--}]}{[\text{MgOx}]} = 2.12 \times 10^{-3}$$

The other values for oxalic acid given in the table were calculated in a similar manner.

With malonic acid the calculation was somewhat simpler because, at the pH of the observations, no appreciable quantity of free malonic acid could be present.

In the case of aspartic acid, it was assumed that the complex formed was



It was assumed that, at pH 8.64 to 9.06, there were no NH_3^+ groups.

With glycine two formulations appeared equally probable. The complex might be $(\text{MgOOCCH}_2\text{NH}_2)^+$ or $\text{Mg}(\text{OOCCH}_2\text{NH}_2)_2$. As in the case of aspartic acid, it was assumed that, at pH 9, there were no NH_3^+ groups.

If each Mg binds one mole of glycine,

$$\text{MgGlyc}^+ = \frac{B' - b'}{1 - b'}$$

whereas if two moles of glycine are bound

$$\text{MgGlyc}_2 = \frac{1}{2} \frac{B' - b'}{1 - b'}$$

TABLE 1

Values for the dissociation constants of magnesium oxalate, magnesium malonate, magnesium aspartate, and magnesium aminoacetate, calculated from the data of Simms*

MAGNESIUM OXALATE			MAGNESIUM MALONATE			MAGNESIUM ASPARTATE			MAGNESIUM AMINOACETATE			
pH	$\sqrt{\mu}$	$K \times 10^3$ (1)	pH	$\sqrt{\mu}$	$K \times 10^3$ (1)	pH	$\sqrt{\mu}$	$K \times 10^3$ (1)	pH	$\sqrt{\mu}$	$K \times 10^3$ (2)	$K \times 10^3$ (3)
2.885	0.26	2.12	5.022	0.27	8.69	8.661	0.28	6.35	8.930	0.28	0.111	31.5
3.182	0.26	2.23	5.260	0.27	8.66	8.847	0.28	5.96	9.065	0.28	0.088	21.9
3.585	0.25	2.31				8.979	0.27	5.26	9.248	0.28	0.091	19.5
2.925	0.19	1.86	5.100	0.20	6.72	8.643	0.20	4.73	9.020	0.20	0.082	20.4
3.479	0.18	1.96	5.436	0.20	7.32	8.884	0.20	4.49	9.128	0.20	0.046	11.2
3.949	0.18	2.05	5.538	0.20	7.60	9.064	0.20	3.98	9.316	0.20	0.059	10.3

$$(1) K = \frac{[\text{Mg}^{++}][\text{A}^{--}]}{[\text{MgA}]} \quad (2) K = \frac{[\text{Mg}^{++}][\text{Glyc}^-]^2}{[\text{MgGlyc}]} \quad (3) K = \frac{[\text{Mg}^{++}][\text{Glyc}^-]}{[\text{MgGlyc}^+]}$$

* These constants are stoichiometric, not thermodynamic.

As may be seen from the table, the latter hypothesis gives a more constant value for K . This is contrary to what has been assumed by Davies (1) for the calcium salt, but it does not appear from his paper that the alternative hypothesis had been considered.

The stoichiometric constants for the dissociation of calcium malonate and oxalate derived in this paper from the data of Simms are much greater than the absolute constants, 16×10^{-4} and 3.7×10^{-4} , respectively, derived by Money and Davies (3) from conductivity data. From the table it will be seen that the values of K decrease as the ionic strength is diminished, but, from the data available, extrapolation to zero ionic strength is not possible. In all probability such values, if obtained, would be closer to those of Money and Davies than are those presented in the table.

SUMMARY

The anomalous effect of magnesium ions upon the dissociation of weak acids is shown to be consistent with the assumption of the formation of slightly dissociated complexes.

REFERENCES

- (1) DAVIES, C. W.: J. Chem. Soc. **1938**, 277.
- (2) GREENWALD, I.: J. Biol. Chem. **124**, 437 (1938).
- (3) MONEY, R. W., AND DAVIES, C. W.: Trans. Faraday Soc. **28**, 609 (1932).
- (4) SIMMS, H. S.: J. Phys. Chem. **32**, 1121, 1495 (1928).
- (5) SIMMS, H. S.: J. Gen. Physiol. **12**, 241 (1928).

NICKEL, CADMIUM, AND LEAD SULFIDES AS CATALYSTS IN THE VAPOR PHASE REDUCTION OF NITROBENZENE¹

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In a previous paper the results of the catalytic activity of cobalt sulfide (3) in the vapor phase reduction of nitrobenzene have been reported. In the present paper the catalytic activity of the sulfides of nickel, cadmium, and lead are dealt with. The object of this study was to investigate the conditions under which the metallic sulfides in question most effectively promote the vapor phase reduction of nitrobenzene, and to compare the results with those obtained when the pure, finely divided metals are used as catalysts.

APPARATUS, PROCEDURE, AND ANALYSIS

The apparatus, general procedure, and analysis were practically the same as that used by Brown and coworkers (2) in previous work.

PREPARATION OF CATALYST

The nickel, cadmium, and lead sulfide catalysts used in this work were prepared by passing hydrogen sulfide gas into the solutions of their respective acetates. In each case the residues were washed with several liters of cold distilled water until all impurities were removed. The pure sulfide residues were dried overnight at 110°C.

NICKEL SULFIDE AS A CATALYST

The nickel sulfide (8.8 g.) was placed in the catalyst tube. Data were collected under the conditions outlined in table 1 to show the effect of temperature on the yield of aniline.

Several runs were made and discarded before the data in table 1 were taken. When a temperature of 282°C. was used, almost colorless aniline was obtained. When a higher temperature was used (296.5°C.), the yield of aniline decreased, but after this point successive runs at temperatures of 290–284°C. gave 97.79 per cent of the theoretical yield of pure aniline.

¹ This paper is constructed from a dissertation presented by Eugene Daniel Raines to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, June, 1938.

When the temperature was dropped to 278–279°C. the yields reached 98.34 per cent of the theoretical value. These data show that, although high temperatures may not give best yields of aniline, the catalyst is activated to the extent that maximum yields of pure aniline may be obtained when much lower temperatures are subsequently used.

Another series of runs was made in order to collect data that would show the effect of rate of hydrogen flow on the yield of aniline. Seven and one-half grams of nickel sulfide catalyst was used at temperatures of 278–280°C. The rate of flow of nitrobenzene was 4.82 g. per hour. With a rate of flow of hydrogen of 9.2 to 11.6 liters per hour, the yield of aniline

TABLE 1

The effect of temperature on the yield of aniline

Weight of nickel sulfide catalyst, 8.8 g.; rate of flow of hydrogen, 11.6 liters per hour;
rate of flow of nitrobenzene, 4.818 g. per hour

NUMBER OF RUNS MADE	TEMPERATURE OF OPERATION	YIELD OF ANILINE
	°C.	per cent
13	279	93.33*
7	282	96.67
11	296.5	93.33
1	290	97.79
3	288	97.79
2	284	97.79
1	274	97.23
8	280	97.23
5	303	95.01
3	308	97.60
4	316	96.90
2	312	95.00
1	279	98.34
5	270	92.73
3	278	98.34

* Each yield of aniline is expressed as the average of the given number of runs.

was from 98.07 to 98.21 per cent. Both lower and higher rates of flow of hydrogen decreased the yields of aniline.

Another series of runs was made over 8.8 g. of the same catalyst at temperatures of 278–280°C. and a rate of flow of hydrogen of 11.6 liters per hour. The rate of flow of nitrobenzene was varied from 3.53 to 12.03 g. per hour. It was found that a maximum yield of aniline of 98.90 per cent was obtained with rates of flow of nitrobenzene of 5.78 to 7.61 g. per hour. The yield of aniline decreased when higher or lower rates of flow of nitrobenzene were used.

A comparison of the results obtained with nickel sulfide and finely divided nickel in the vapor phase reduction of nitrobenzene to aniline, when

the best working conditions were used, is given in table 2. It is seen from these data that higher yields of aniline are obtained with a nickel sulfide catalyst than with a metallic nickel catalyst. It is of interest to note that the best temperature of operation for the nickel sulfide catalyst is 87°C. higher than for metallic nickel. As catalyst for the production of a given weight of aniline only about one-fourth as much nickel sulfide as metallic nickel was required.

CADMIUM SULFIDE AS A CATALYST

The catalytic activity of cadmium sulfide in the vapor phase reduction of nitrobenzene was investigated between temperatures of 289° and 400°C. The catalyst was permanently killed at temperatures of 361°C. and above.

With 14 g. of cadmium sulfide catalyst, a rate of flow of hydrogen of 12 liters per hour, and a rate of flow of nitrobenzene of 2.9 g. per hour at 346°C., the yield of aniline was 83.72 per cent. This is the highest yield obtained over cadmium sulfide. This indicates that cadmium sulfide is a

TABLE 2

Comparison of nickel and nickel sulfide as catalysts

CATALYST	METALLIC NICKEL FROM OXIDE (2)	NICKEL SULFIDE FROM NICKEL ACETATE
Weight of catalyst.....	16 g.	8.8 g.
Operation temperature.....	192°C.	278-280°C.
Liters of hydrogen per hour.....	17	11.6
Grams of nitrobenzene per hour.....	3.1-3.8 g.	5.78-7.61 g.
Yield of aniline in per cent of theoretical yield	95.8	98.90

poorer catalyst for the vapor phase reduction of nitrobenzene than finely divided metallic cadmium (1), which gives quantitative yields of pure aniline.

LEAD SULFIDE AS A CATALYST

After making a study of the effect of change of temperature and the rate of flow of hydrogen and nitrobenzene over 16.2 g. of a lead sulfide catalyst, a 98.2 to 98.45 per cent yield of aniline was obtained. The conditions were 308° to 310°C. with a rate of flow of 24.8 liters of hydrogen and 3.56 g. of nitrobenzene per hour. At 308° to 310°C. the aniline was water-white. When temperatures above 312°C. were used there was a noticeable decrease in the quantity of aniline produced.

The lead sulfide catalyst became more active with use, as long as the best working conditions were used. Excessive amounts of hydrogen seemed to inactivate the catalyst. When the lead sulfide was taken from the catalyst tube for examination, it was found to have been partly re-

duced. Balls of lead less than 1/36 in. in diameter were picked from the grains of lead sulfide.

Lead sulfide is a good catalyst for the vapor phase reduction of nitrobenzene. The behavior of the lead sulfide catalyst was in many ways similar to that of a metallic lead catalyst (4). The lead sulfide catalyst gave practically no azobenzene; however, a yield of azobenzene as high as 30 per cent may be obtained over a freshly prepared metallic lead catalyst.

SUMMARY

1. Nickel sulfide as a catalyst: (1) Data have been collected which show that yields of aniline as high as 98.90 per cent of the theoretical yield were obtained over a nickel sulfide catalyst at 278° to 280°C. (2) A nickel sulfide catalyst is a better producer of high yields of water-white aniline than is pure, finely divided metallic nickel.

2. Cadmium sulfide as a catalyst: (1) Cadmium sulfide as a catalyst in the vapor phase reduction of nitrobenzene was thoroughly investigated. Under optimum working conditions (temperature, rate of nitrobenzene flow, and rate of hydrogen flow) the maximum yield of aniline was 83.72 per cent. (2) Cadmium sulfide is very sensitive to temperature changes. It was permanently killed at a temperature of 361°C. or above. (3) Cadmium sulfide is not a good catalyst for the reduction of nitrobenzene to aniline, in that it gives low yields of aniline and a colored product.

3. Lead sulfide as a catalyst: (1) When lead sulfide was used as a catalyst at 308° to 310°C., yields of aniline as high as 98.45 per cent were obtained. (2) The activity of a lead sulfide catalyst is similar to the pure lead catalyst, in that the highest aniline yields are obtained at 308° to 310°C. and the activity of both catalysts increases with use as long as the optimum working conditions are maintained.

REFERENCES

- (1) BROWN, O. W., AND HARTMEN, R. J.: *J. Phys. Chem.* **34**, 2651-65 (1930).
- (2) BROWN, O. W., AND HENKE, C. O.: *J. Phys. Chem.* **26**, 161-75 (1922).
- (3) GRIFFITHS, F. A., AND BROWN, O. W.: *J. Phys. Chem.* **41**, 477-84 (1937).
- (4) MADENWALD, F. A., HENKE, C. O., AND BROWN, O. W.: *J. Phys. Chem.* **31**, 864 (1927).

COMMUNICATION TO THE EDITOR
THE SOLUBILITY OF CALCIUM BICARBONATE. II
PARTIAL PEPTIZATION¹

One of my colleagues noted that in my report on the solubility of calcium bicarbonate (*J. Phys. Chem.* **42**, 971 (1938)) I did not mention the possibility that part of the salt might be peptized, and part might be in true solution. This should be considered, since it is well known that gelatin and certain soaps fall into this class, although in these cases the major portion is peptized, not dissolved, by the water.

Experiments with collodion membranes similar to the previous ones were carried out, except that the original solutions were filtered free from visibly suspended calcium carbonate, and unit concentrations were determined for the diffusand and the diffusate. If part of the calcium bicarbonate were merely peptized, the total calcium concentration at equilibrium would be higher in the diffusand than in the diffusate, which fact can be seen by examining the general expression for a Donnan equilibrium.

A solution with a concentration of 68.8 mg. per 100 cc. (calculated as calcium carbonate and discounting the ordinary solubility of this salt) was used. The final concentration inside the membrane was 9.64 mg. per 100 cc.; that outside was 9.63 mg. per 100 cc. A second run with a different membrane and an original concentration of 70.5 mg. per 100 cc. gave values of 8.89 and 8.91 mg. per 100 cc., respectively. Thus, within the error of analysis, all of the calcium bicarbonate seems to be in true solution.

Since the green of the streams referred to in the first paper seems not to be due to colloidal calcium bicarbonate, we are planning to obtain samples of the water to determine the source of the color, if possible.

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¹ Received November 1, 1938.

NEW BOOKS

Unit Processes in Organic Synthesis. By P. H. GROGGINS. Second edition. 741 pp. New York: McGraw-Hill Book Company, Inc., 1938. Price: \$6.00.

In the preface to the first edition the author states that his purpose is "to present in a systematic manner the principles and practice of the more important and well-defined reactions in organic synthesis" and to correlate these under the term "unit processes," as the multifarious physical operations of chemical industry had been previously correlated under the term "unit operations." The success of this idea was proved by the widespread and enthusiastic reception of the first edition. But the rapid growth and ever changing emphasis of organic syntheses necessitate frequent revisions of such an undertaking. This has been admirably accomplished in the second edition of this valuable book.

Without change in the general plan of the book the several chapters on nitration, amination, hydrolysis, sulfonation, oxidation, esterification, and the Friedel-Crafts reaction have been enlarged and brought into line with current developments, especially with relation to the increased emphasis on aliphatic chemistry. The unit processes of halogenation and hydrogenation are given new theoretical treatment from the thermodynamic point of view. An excellent section on coupling has been added to the chapter on diazotization, and the chapter on alkylation has been substantially revised and enlarged. The marked increase in number and importance of the synthetic plastics is reflected in the complete rewriting and enlargement of the chapter on polymerization, although it is to be regretted that the special case of simple condensation so widely used in the manufacture of dyes and intermediates is not adequately treated. All the other common unit processes have been given complete treatment, with the minor exceptions of nitrosation and acylation.

The book is rendered more authoritative because it is a collaborative effort of twelve experts, all well-known to American chemistry, with P. H. Groggins acting as Editor-in-chief. This volume exhibits the usual careful workmanship of all the members of the McGraw-Hill Chemical Engineering Series. It is indispensable to workers in the field of organic technology and should be equally useful to the pure organic chemist, because of its valuable correlation of synthetic methods.

RALPH E. MONTONNA.

Introductory Quantum Mechanics. By V. ROJANSKY. New York: Prentice-Hall, Inc., 1938.

The extraordinary success that has attended the application of the methods of quantum-mechanical theory to chemical as well as physical problems (if such a distinction may still be supposed to exist) has brought with it the necessity for renewed activity in the study of certain branches of pure mathematics which have been largely overlooked in the curricula of science students. As a consequence a considerable portion of any course in quantum mechanics must be devoted to the study of linear operators, matrices, partial differential equations, expansions in series of orthogonal functions, group theory, etc. Rojansky's book is designed to facilitate the study of this mathematical framework in a reasonably elementary and yet comprehensive way. It does not go very thoroughly into any of the special fields of application such as atomic or molecular theory, metallic conductivity, etc., but develops strictly only the basic theory which is common to all of these fields.

In the opinion of this reviewer Rojansky's text fills in an admirable manner a need that has existed for a long time in the literature of quantum mechanics. The whole book shows evidence of a careful selection and arrangement of material as well as choice of explanatory method. While making few demands on the previous mathematical training of the student, it still manages to cover most of the material necessary for a good foundation in the basic principles of quantum mechanics. The numerous problems are easy but not trivial, and seem to be well chosen for their explanatory character. In view of the absence of detailed applications the book does not furnish a basis for a comprehensive course of study in any given field of quantum mechanics, and should be used in conjunction with some book or set of lectures covering the field in which the student may be particularly interested. For one desirous of attaining a thorough grounding in quantum mechanics and its applications to physicochemical problems, the reviewer can give no better advice than to study Rojansky for general theory and Pauling and Wilson (McGraw-Hill Book Co., 1935) for applications, and especially to *work the problems in both books*. With this foundation he can forge into the broad fields of quantum mechanics on his own with a sure footing.

E. L. HILL.

Inhibitorwirkungen. Eine Darstellung der negativen Katalyse in Lösungen. By K. WEBER. Die chemische Analyse, herausgegeben von W. Böttger, Band 50. 25 x 16 cm.; xii + 191 pp. Stuttgart: F. Enke, 1938. Price: unbound, 16.60 RM.; bound, 18.20 RM.

The subject of reaction inhibition has recently attracted much interest, and a book on the field by K. C. Bailey (in English) appeared a short time ago. The present volume deals with the subject largely from the physicochemical point of view and is a useful supplement to the literature. In confining the field to solutions the author has had to omit much material of interest, so that the book cannot claim to cover the whole field of anticatalytic phenomena. The main sections are on the quenching of fluorescence, and on retardation in photochemical, autoxidation and thermal reactions, and general inhibition reactions. In each section the more important typical reactions are considered, and on the whole a good balance of space is maintained. In some cases more information would have been welcome, but in the limitations of the space available to him the author has been able to put before the reader the important lines of research in his field. His attempt to treat the various phenomena from a general standpoint is of considerable interest, and will undoubtedly lead to clarification of ideas in this field. The significance of the phenomena in analytical chemistry is pointed out in each case. Important technical aspects, such as the oxidation of oils, the perishing of rubber, and the combustion of hydrocarbons, are taken into consideration. The book gives a very compact and useful survey of the field and can be recommended.

J. R. PARTINGTON.

Die Darstellung der Metalle im Laboratorium. By H. FUNK. Enke's Bibliothek für Chemie und Technik unter Berücksichtigung der Volkswirtschaft, herausgegeben von L. Vanino, Band 25. 22 x 14 cm.; viii + 183 pp. Stuttgart: F. Enke, 1938. Price: unbound, 8.00 RM.; bound, 9.80 RM.

The object of the present book is to collect in a handy form the modern information on the preparation of the metals in a state of purity on the laboratory scale. It is very practical, and the experimental details are sufficient to enable a chemist familiar with ordinary laboratory operations to carry out the processes described. In research in physics and physical chemistry it is often necessary to have available

pure specimens of metals, including those not very well known and not purchasable on the market, and the chemist to whom the preparation of these materials is entrusted will be very grateful for such a book as this. Full references to the literature are given, and, in addition to the preparative details, the book gives much useful information on the properties and uses of the metals. It includes the rarer metals such as beryllium, cesium, gallium, germanium, hafnium, indium, the platinum metals, thallium, vanadium, etc. The apparatus is described in sufficient detail, with dimensions, etc. In addition to its professed purpose, the book may be strongly recommended to teachers of inorganic chemistry, since it gives much information on the metals that cannot easily be found otherwise. It is a book that should be in every chemical and physical laboratory.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 63: Ruthenium. 26 x 18 cm.; pp. xx + vi + 124. Berlin: Verlag Chemie, 1938. Price: 16.50 RM.

A wrapper on this part of the *Handbuch* announces that the treatment of the platinum metals is now in hand and that the volumes of the section of the work dealing with the platinum metals will appear very shortly. This is a very welcome statement, since the information on these important metals has not so far been presented in a form that is sufficiently critical to meet modern requirements, and the recent important technical developments are still without an adequate review in sufficient detail. The present monograph, which is complete in itself, deals with ruthenium. The history, occurrence, and extraction of the element are deferred for the forthcoming volume on platinum, and the present section deals with the physical and chemical properties of the element and its compounds. In all sections an attempt is made to differentiate between compounds the existence of which is established without doubt and those which are still without adequate characterization. Thus, for example, it is stated that the oxides RuO_2 and RuO_4 , the chlorides RuCl_2 , RuCl_3 , and RuCl_4 , and the carbonyls $\text{Ru}_2(\text{CO})_9$ and $\text{Ru}(\text{CO})_5$ are the only ones definitely established, and that the only definite sulfide is RuS_2 . All the other, doubtful, compounds are fully treated. The information includes the complex compounds. Modern work is fully taken into account. The monograph is an important and thoroughly satisfactory contribution to the literature of inorganic chemistry.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 27: Magnesium. Teil B. Lieferung 2. 26 x 18 cm.; pp. 201-330. Berlin: Verlag Chemie, 1938. Price: 15.75 RM.

Compounds of magnesium with sulfur, selenium, tellurium, boron, and carbon, including oxy salts, fall for treatment in this section. Magnesium sulfate and its hydrates come in for very detailed treatment, in seventy-five pages. The section on the boride, Mg_2B_3 , is of interest in relation to boron hydrides, which are now the subject of physicochemical investigation. Magnesium carbonate and the basic carbonates, which are of technical and pharmaceutical interest, receive full treatment. A critical survey of the physical, physicochemical, and chemical properties of the substances is very complete and authoritative. This section is a notable contribution to chemical literature, and fully maintains the high standard that characterizes the whole handbook.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 25: Cesium. Lieferung 1. 26 x 18 cm.; 104 pp. Berlin: Verlag Chemie, 1938. Price: 12.00 RM.

The present section deals with the occurrence of cesium, the production of its compounds from the minerals, and the preparation and properties of cesium metal. Cesium occurs in useful amounts in some varieties of beryl, but pollux (pollucite), an aluminosilicate of cesium, is still the only rich source. This mineral occurs in Elba and in some parts of the United States, and contains about 30 per cent of cesium. The metal has now a very considerable technical interest in the production of photo cells and radio tubes, and the American deposits of pollucite, it is stated, are now being worked. Considerable quantities of cesium compounds are also produced in Russia. It is stated that the import of cesium compounds to the United States is probably only from Germany. The physical properties of cesium, which are rather fully known, are dealt with in full detail, with tabulation of numerical data and spectrum diagrams. The photoelectric properties receive particular attention, since these are at the basis of television outfits, and the present section is, therefore, in the center of modern interest. The whole presentation is full, critical, and up-to-date, and is likely to appeal to wide interests.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 22: Kalium. Lieferung 5. 26 x 18 cm.; pp. 933-1074. Berlin: Verlag Chemie, 1938. Price: 19.50 RM.

The compounds of potassium dealt with in this part are the acid acetate, oxalates, tartrates, silicates, and compounds with phosphorus, arsenic, antimony, and bismuth, including oxy salts. The compounds thus include a number of salts and double salts with organic acids which are of considerable technical interest. The treatment is based, whenever possible, on modern physicochemical foundations. Many good phase-rule diagrams are given. In this way much of the confusion in the literature, e.g., that concerning the oxy salts of antimony and bismuth, is cleared up. Technical progress is adequately described and very full accounts of physical and chemical properties are provided. The treatment is critical, and attention is frequently drawn to outstanding difficulties, such, for example, as the discrepancy between the crystallographic results and well-established physicochemical conclusions relating to the ion BF_4^- in KBF_4 . In the section on hypophosphates the recent work establishing the formula $\text{H}_4\text{P}_2\text{O}_6$ for the acid is mentioned only, with a reference to the volume on phosphorus, and alternative formulas for the salts are still given.

J. R. PARTINGTON.

Outlines of Biochemistry. By ROSS AIKEN GORTNER. Second revised edition. 23 x 15 cm.; xx - 1017 pp. New York: John Wiley and Sons, Inc., 1938. Price: \$6.00.

Since the publication of the first edition of the *Outlines of Biochemistry* nine years ago, old fields of biochemistry have greatly expanded and new fields have been opened up. The author has brought into the new edition so much of this work that it has been necessary to enlarge the book by more than two hundred pages. The one thousand seventeen pages have been kept in one volume, a very desirable feature. Three chapters have been added and many of the topics have been largely rewritten. A total of more than twelve hundred new references, dated since 1929, has been included; the number of figures has been increased from one hundred thirty-three to one hundred sixty-five and the tables from sixty-seven to eighty-six.

The new book is divided into the same general parts found in the first edition: I, the colloid state of matter, 348 pages; II, proteins, 226 pages; III, carbohydrates, 138 pages; IV, lignin and the tannins, 17 pages; V, plant and animal pigments, 35 pages; VI, the lipids and essential oils, 66 pages; VII, the biocatalysts, 122 pages.

The three new chapters are: V, oxidation-reduction, written by H. B. Bull; XXXI, the flavins; and XXXVI, the hormones, written with the cooperation of L. S. Palmer. Oxidation-reduction is given the usual treatment for chemistry students, with little attempt at biological application. The relation of the flavins to vitamins and enzymes is discussed in five pages. Chapter 36 gives a good brief review of both plant and animal hormones.

Among additions to the colloid section are Svedberg's molecular weight studies, much new electrokinetic data, surface film work, and new terms like thixotropy and coacervation.

The protein section is greatly changed with the zwitter-ion treatment of amino acids, the new amino acids and their value in nutrition, new studies on protein structure, intermediates of amino acid metabolism, etc.

The newer formulas and proposed structures of carbohydrates are included in section III. The discussion of lignin is entirely new.

The chief addition to the lipid section is extensive new data on synthetic glycerides, fatty acid structures and nutrition, and antioxidants.

The completely rewritten chapter on vitamins is one of the best. The discussion of the chemical nature of the enzymes greatly enlarges that chapter.

To avoid undue length the author has limited the more strictly physiological subjects like photosynthesis, respiration, permeability, etc.

In certain fields, such as resistance of plants to drought and cold, the author may sometimes give wrong impressions by limiting his discussions to purely biochemical studies. Physiologists are generally in agreement that resistance to drought and cold is dependent on so many factors, including structure, that no one measurable characteristic is likely to be proved "all important."

This edition is a distinct improvement over the first and should be even more widely used than that very popular volume.

GEORGE O. BURR.

Chemische Spektralanalyse. By W. SEITH AND K. RUTHARDT. 20 x 14 cm.; vi + 103 pp. Berlin: Julius Springer, 1938. Price: 7.50 RM.

This is the best textbook on practical spectrochemical analysis that has yet appeared in the German language. Arranged in a series of twenty-two practical lessons or exercises, the various sections follow each other in easy and logical progression. The necessary apparatus, test pieces, and reference books required are listed at the commencement of each lesson. The instructions are concise, complete, and clear, and particulars of some representative modern methods are included. Absorption spectrophotometry is dismissed in one short lesson, but qualitative and quantitative spectrochemical analysis, both visual and photographic, are adequately dealt with in so far as they are practised in the author's country. Some use is made of the nomenclature and of the energy level diagrams of modern atomic spectrum theory, but the space devoted to this is necessarily very restricted.

The book suffers from one grave defect,—it ignores with a completeness unique in publications on this subject all information that cannot be referred to German sources; otherwise it might have been the best introductory textbook on the subject that has yet appeared in any language.

F. TWYMAN.

Chemical Reactions Involving Solids. A General Discussion held by the Faraday Society. 25 x 16 cm.; 266 pp. London: Gurney and Jackson, 1938. Price: 12s. 6d.

The thirty-five papers included in this discussion cover many aspects of the subject of reactions involving solids. These have been satisfactorily grouped into five sections. The first part (Ia) deals with physical aspects of the subject and includes summaries of the present state of knowledge regarding electron levels in crystals. This is followed (part Ib) by a series of eight papers on the mechanism of the transport of atoms and ions through solids. Part II of the discussion is treated under three headings: (1) "Photochemical Processes," which includes photoprocesses in solid solution in relation to the production of *Farbzentren* and many interesting papers and discussions on the nature of sensitization of solids, especially in relation to photographic processes. (2) "Thermal Reaction and Detonation in Solids," which deals with the kinetics of decomposition and dehydration reactions, and the processes giving rise to detonation and explosion. (3) The last part of the discussion (II) is confined entirely to papers on the reactivity of solid carbon, and bears little relation to the foregoing parts. This includes some nine papers on inter-layer lattice compounds, the graphitic salts, and the kinetics and mechanism of carbon oxidation.

The papers provide an excellent survey of many of the aspects of the chemistry of solids. This volume should be in the hands of everyone interested in the solid state.

C. E. H. BAWN.

Reaction Kinetics. A General Discussion held by the Faraday Society, September, 1937. 25 x 16 cm.; 268 pp. London and Edinburgh: Gurney and Jackson, 1938. Price: 12s. 6d.

This book serves the dual purpose of marking the present stage of progress in the theoretical and experimental fields in reaction kinetics and of pointing out the ways in which this may well advance. The subject, by the very fact that the various aspects are presented by enthusiasts in their own work, is given an atmosphere that can rarely be captured in textbooks. Reading the reports and the discussion one can sense the living nature of the material, and from this point of view alone the book is admirable for its inspiration. But not in this alone lies the excellence of this book; it also provides clear surveys of the present state of experiment and theory. In the section on theories of activation energy and reaction velocity the underlying principles for the construction of potential energy surfaces for reacting systems are discussed, and the more empirical methods which have been used to obtain an understanding of chemical inertia are described in some detail. The reviews and discussions of the collision theory and the transition state method of treating reaction kinetics are of particular value and interest. The essential differences in approach, the interrelationship of the two theories, and their strengths and weaknesses as theoretical tools are very clearly emphasized.

The later sections contain subjects which appear at first sight to be widely divergent, such as the kinetics of diene synthesis, the influence of hydrostatic pressure on reaction velocity, linear free energy relations in rate and equilibrium phenomena, and proton transfer reactions; however, all these subjects either fall into place in a general scheme in the light of the earlier sections of the discussion or present problems for future research.

The influence of various groups and different structures on the velocity of reaction of series of organic compounds has long been a study of great interest to organic chemists, and reviews are presented in which these questions are discussed. For example, when substituents are introduced into benzene derivatives the change in the velocity of reaction of these compounds is found to be due for the most part to changes in the activation energy. Changes in the velocity constants of a series of

chemical reactions are often found to be related to changes in the equilibrium constants of the same or of a very similar series of reactions. This indicates a very important approach to the understanding of the factors influencing the reactivity of organic compounds. In the field of negative ion reactions it has been possible to trace a relationship between the mechanism on the one hand and the chemical structure of the reactants and the physical conditions of reaction on the other. In both these fields it is just beginning to be possible to connect these relationships with the factors influencing chemical inertia.

The reviewer feels that in this book not only have certain aspects of the reaction velocity problem been clarified, but also a great stimulus has been given to further work in this field.

M. G. EVANS.

An Introduction to Industrial Rheology. By G. W. SCOTT BLAIR. 12 x 19 cm.; xiii and 143 pp. London: J. & A. Churchill, 1938. Price: 7s. 6d.

As the author points out, a great number and variety of materials of technical importance flow in certain conditions of temperature, stress, or moisture content. In many cases, however, the flow is not of the simple type called "Newtonian" by the rheologists, in which the smallest stress causes irrecoverable deformation and the stress is directly proportional to the velocity gradient. The deviations from this type are numerous: flow may not begin at all until a certain stress—the "yield value"—has been exceeded; the stress may not be in linear ratio to the velocity gradient but may be a function of it, and combinations of these two types are frequent. The systems may, though apparently limpid liquids, possess measurable rigidity, while a combination of high rigidity and viscosity determines the behavior of, e.g., flour dough, the successful mathematical formulation of which is due to the author and Schofield.

The ways in which these anomalies manifest themselves when "apparent viscosities" are measured by the methods applicable to normal liquids, the formulae proposed by a number of investigators for anomalous flow and the special types of apparatus suitable for measuring it, are set forth by the author concisely, clearly, and without excessive mathematical apparatus. Workers having to control the properties of materials as divergent as paints, tooth pastes, flour doughs, or clays will find full guidance in these chapters.

The two types of viscous behavior depending on the immediate previous history—thixotropy and dilatancy—are discussed and are shown to be of technical interest. The last three of the twelve chapters present flow in aspects unfamiliar to the chemical reader, and give a summary of the achievements and promise of rheology.

The book certainly fills a gap in the literature of physics. It should find its way into any laboratory which boasts of Ostwald or Redwood viscometers, as well as many others.

E. HATSCHEK.

Die analytische Verwendungen von o-Oxychinolin ("Oxin") und seiner Derivate.

By R. BERG. 24 x 16 cm.; xi + 114 pp. Stuttgart: Ferdinand Enke, 1938. Price: unbound, 11 RM.; bound, 12.40 RM.

This monograph maintains the high standard of the series on chemical analysis edited by Professor W. Böttger. It is an extension of Professor Berg's 1935 publication, and the necessity for revision after such a short interval is evidence of the manifold uses to which "oxine" is still being put, although it is twelve years since it was first systematically applied to analysis.

A valuable feature of the work is the author's fuller details (many hitherto un-

published) for a number of the methods; these will be welcomed by analysts who have had difficulty with some of the procedures. Microchemical applications, both qualitative and quantitative, have been extended, and both these and macro methods have been adapted to a wide variety of technical processes. The colorimetric methods are of interest, but their utility is often restricted by their lack of specificity.

Thirty-one metals now come under the sway of "oxine," and the different conditions of precipitation lead to many useful separations which are clearly set out. In some cases, however, e.g., that of lanthanum and niobium (columbium), the metals cannot be separated from their congeners, and the methods are of limited value.

A minor, but annoying, defect is the carelessness in the spelling of names: Pregel for Pregl (page 33), Nieszner for Niessner (page 28), and even (page 3) Berd for Berg! The index rectifies these errors but adds others. Also, on page 2 the *Journal of the American Chemical Society* is given instead of the English *Journal of the Chemical Society*, and on page 51 the converse error occurs.

A. D. MITCHELL.

The Oxidation States of the Elements and their Potentials in Aqueous Solutions. By W. M. LATIMER. 352 pp. New York: Prentice Hall, Inc., 1938. Price: \$3.00.

This book gives more than the title indicates. As stated by the author, the primary object of the work is to gather together the large mass of free-energy data which is scattered throughout the literature and to present it in a simple form as an aid in the interpretation of inorganic chemistry. Moreover, solubility products and the dissociation constants of many acids, bases, and complex ions have been included. In calculating many new free energies from reaction heats Professor Latimer has drawn largely upon his own experimental work on the entropies of solids and aqueous ions. The author has succeeded well in the task that he set himself and has presented us with an authoritative text, which satisfies a long-felt need in physical, inorganic, and analytical chemistry. Anyone interested in the states of oxidation of elements will find the wealth of information to be obtained from this text invaluable.

The first chapter is introductory and deals with units, conventions, etc. Unfortunately, the expression of the activity as given on page 2 (ninth line) is not very exact. The second chapter is of a general theoretical nature and discusses briefly the relation between oxidation potentials on the one hand and ionization potentials, electron affinities, hydration energies, and lattice energies on the other. This chapter might be enlarged with advantage; reference could have been made to R. W. Gurney's book *Ions in Solution*. Although it is specified in the title of the book that only potentials in aqueous solutions are considered, the solvent effect might have been discussed in the second chapter.

The remaining nineteen chapters deal with an exhaustive treatment of the states of oxidation of the various elements. On page 29 reference might have been made to Heyrovský's theory of the overpotential of hydrogen and deuterium. Especially in the chapter on carbon, results obtained with the dropping mercury electrode could have been referred to with advantage. The book is remarkably free from misprints; on page 189 the reviewer noticed that Thiel's name was misspelled several times. The summaries of oxidation potentials, free energies of formation, equilibrium constants, activity coefficients, and entropy values in the appendices are valuable.

This book, undoubtedly, will receive the recognition and wide circulation that it deserves.

I. M. KOLTHOFF.

The Physical Properties of Colloidal Solutions. By E. F. BURTON. 23 x 16 cm.; viii + 235 pp. London: Longmans, Green and Co., 1938. Price: 15s. 0d. net.

The new edition of this well-known textbook has been very largely rewritten and much new material introduced. As in previous editions the historical method of approach has been employed to great advantage, and numerous verbatim extracts from papers of historical importance have been most skillfully introduced into the text.

The treatment of the Brownian movement, particle distribution, and fluctuations is much more complete than is usually found in a textbook of this type, while the chapter summarizing the various available methods for the determination of Avogadro's number, emphasizing, in a quotation from W. Ostwald, that the concordance of the results provides one of the strongest proofs of the objective reality of the atomic hypothesis, is specially interesting. While one feels at times that the author's own conclusions are sometimes given undue emphasis—the "conspiracy of opposition" (page 100) is perhaps not entirely wanton—the attitude adopted is certainly preferable to any colorless attempt at complete impartiality.

The chapter on electrokinetic phenomena, and to a less extent that on coagulation, have an "old-fashioned" flavor, and are, in the reviewer's opinion, not of the same standard as the earlier parts of the book. The transport method of electrophoretic investigation is ignored, as also are important investigations into the theory of the moving boundary method. The frequently observed unequal motion of the two boundaries is provisionally attributed to "settling" and is said (page 175) to be immaterial provided the mean is taken; in fact the Kohlrausch-Weber theory shows that it is an intrinsic phenomenon and that the mean is *not* the correct value. The difficulties arising from inhomogeneity of the potential gradient are dismissed too summarily. Figure 33 (c) is misleading, as the flow distribution drawn is not that given by equation 31, and no mention is made of the fact that, with a cell of the dimensions shown in figure 33 (a), this equation would itself be many per cent in error.

While numerous similar points of criticism can be found, the fact remains that the book is stimulating and informative; it is a book to read.

D. C. HENRY.

International Annual Tables of Constants and Numerical Data. Vol. XI, Part I (1931-34) and additional separate monographs of Volumes XI and XII. Published under the auspices of the International Council of Scientific Unions and of the International Union of Chemistry. Paris, France: Hermann et Cie. Price: Vol. XI, Part I, 290 francs.

Volume XI, Part I, of these annual tables contains twenty-five sections covering the following subjects for the years 1931-34: 1. General Indications. 2. Universal Constants. 3. Elasticity, Compressibility. 4. Thermal Expansion. 5. Density. 6. Viscosity. 7. Surface Tension. 8. Heat Conductivity. 9. Specific Heat. 10. Free Energy, Heat Content, Entropy. 11. Activity. 12. Thermochemistry, Calorimetry. 13. Vapor Pressure, Boiling Temperatures. 14. Gas Laws. 15. Acoustics. 16. Diffusion, Osmosis. 17. Volta Effect, Triboelectricity. 18. Thermoelectricity. 19. Piezoelectricity. 20. Metallic Electrical Conductivity. 21. Superconductivity. 22. Dielectric Constants, Dipole Moments. 23. Paramagnetism, Diamagnetism. 24. Ferromagnetism. 25. Hall Effect. Section 26, Raman Effect, and section 26, Rotatory Power, appeared as separate monographs.

Volume XII, Part I, covering all of these subjects for the years 1935-36 will appear

shortly. Part 2 of Volume XI and Part 2 of Volume XII will be amalgamated in one edition covering the six-year period. This will also be true of Part 3.

The following monographs from Parts 2 and 3 of the combined volumes have appeared: 31. Molecular Spectra,—Part I, Diatomic Molecules; Part 2, Tri- and Poly-atomic Molecules. 38. Faraday Effect. 39. Magnetic Birefringence. 40. Electrical Birefringence. 41. Photoelectricity. 60. Electromotive Forces. 70. Combustion of Gases. A monograph on deuterium, which will be welcomed by workers in the field, has also been issued.

The International Council is to be commended for making sections of the bound volumes available in the form of monographs so that specialists may obtain them without having to buy the bound volumes.

L. H. REYERSON.

A STUDY OF THE HYDROGEN-BROMINE REACTION UNDER THE INFLUENCE OF ALPHA PARTICLES FROM RADON¹

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The thermal rate of formation of hydrogen bromide from its elements was first accurately studied by Bodenstein and Lind in 1906 (1). They found that the rate of reaction could be expressed by the following equation,

$$\frac{d(2\text{HBr})}{dt} = \frac{k(\text{H}_2)\sqrt{(\text{Br}_2)}}{m + \frac{(2\text{HBr})}{(\text{Br}_2)}}$$

m being a constant independent of temperature and having a numerical value of 5.

The interpretation of this reaction was arrived at independently by Christiansen (3), Polanyi (9), and Herzfeld (4). The mechanism may be designated in the following steps:



The photochemical combination of hydrogen and bromine was studied by Bodenstein and Lütke Meyer (2), who found that the reaction proceeded according to the following equation:

$$\frac{d(\text{HBr})}{dt} = \frac{k\sqrt{I}(\text{H}_2)}{m' + \frac{(\text{HBr})}{10(\text{Br}_2)}}$$

¹ This article is based upon a thesis submitted by Earl F. Ogg to the Faculty of the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, September, 1930.

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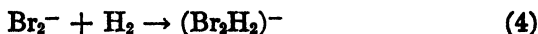
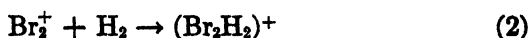
This is quite similar to the one expressing the rate of thermal combination. In this instance, however, the bromine atoms are produced in larger numbers, not only thermally, but by the reaction



This is then followed by the same series of thermal reactions as before. The range of temperature in which they worked was 160° to 218°C.

The only previous work with radioactive agents was done by Lind (5) in 1911. He found that the beta and gamma radiation that he could command had practically no power to cause hydrogen and bromine to combine, but that measurable reaction occurred under alpha-particle radiation. At room temperature and with stoichiometric proportions of hydrogen and bromine, a yield of 0.54 molecule of hydrogen bromide per ion pair was obtained.

It was thought possible that bromine possessed an affinity for electrons; if so it would be able, under alpha-particle radiation, to form both positive and negative ions, which upon neutralization would give hydrogen bromide according to the following scheme:



A series of reactions of this kind would lead to a maximum of four molecules formed per ion pair, which is twice the number in the simplest stoichiometric mixture (7). It was thought that even though an *M/N* yield of 0.54 was obtained at room temperature, possibly at some higher temperature the yield would approach 4, thus lending support to the clustering mechanism.

EXPERIMENTAL PROCEDURE

The bromine employed for these experiments was Baker's c.p. analyzed. It was distilled twice over potassium bromide in order to remove any chlorine which might be present. The hydrogen used was formed by electrolysis of a 40 per cent potassium hydroxide solution, electrolyzed between nickel electrodes. The gas so produced was led through a heated tube containing palladium asbestos for the conversion of any oxygen present to water vapor. Any moisture so formed was then removed by passage through concentrated sulfuric acid. Excessive drying

was considered unnecessary, since Lind (1) found that the speed of the thermal reaction was not influenced by the presence of water vapor.

The glass bulbs in which the reactions were carried out were of approximately 40 cc. capacity. They were provided with capillary tubing on each end, the thick wall of which was drawn down so as to facilitate their sealing off with a torch. The calculated quantity of pure bromine to furnish 0.5 atm. in the bulb was weighed out in a small thin-walled glass capsule, which was subsequently sealed. The capsule, together with the radon capsule, was then placed in the glass bulb, and the latter was sealed onto the hydrogen filling apparatus at A, as shown in figure 1. Hydrogen

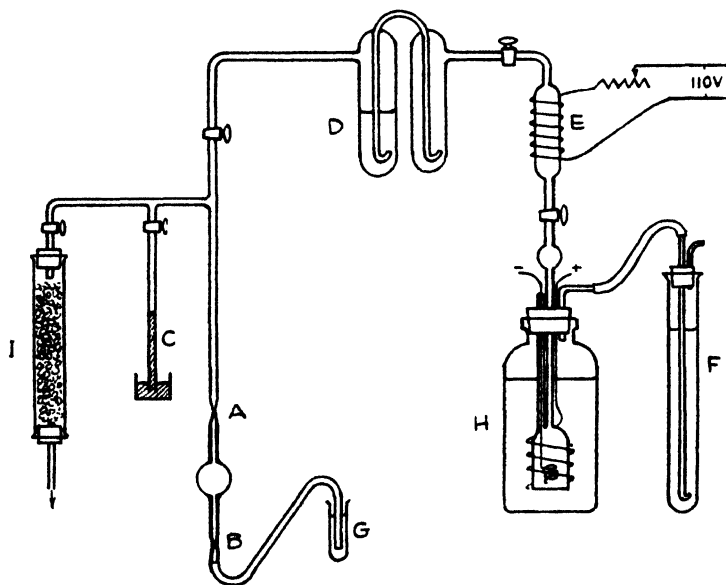


FIG. 1. Diagram of the apparatus. D, sulfuric acid drying tube; E, heated tube for palladium asbestos; F, pressure column for oxygen exit; G, sulfuric acid outlet for hydrogen; H, hydrogen generator; I, soda-lime tube to vacuum.

was passed through the bulb for 15 to 20 min., after which the capillary was sealed off at B. The bulb was then evacuated three or four times with a water pump and permitted to refill each time with hydrogen. Finally the pressure was adjusted to 0.5 atm., as indicated by the height of the mercury column C, and the bulb was sealed off at A. Upon shaking the bulb vigorously, the thin-walled capsules of bromine and radon were shattered, after which the mixture could be placed in an oven at the desired temperature. A blank thermal run accompanied each radon run (except in the experiment at the lowest temperature of 40°C., at which temperature the thermal combination would be negligible). In this way

the amount of reaction due to temperature alone could be compared to the total reaction brought about by alpha particles plus thermal reaction.

The experiments performed at temperatures below 200°C. were carried out in a Freas electric oven, which held the temperature to within 2°C. Those performed above 200°C. were carried out in a small aluminum oven specially constructed for the purpose. Its temperature was controlled by means of a bimetallic contact.

When the duration of an experiment was relatively long, using temperatures up to 200°C., the bulbs were placed in the oven immediately upon breaking the radon capsule. In calculating the amount of ionization over a long period very little error would result in assuming that radioactive equilibrium was established immediately between radon and its decay products. In the case of the shorter runs, however, immediately after shattering the capsules the bulb was immersed in a salt-ice mixture for 4 hr. at a temperature of -10° to -15° C. This served to freeze out the bromine while permitting the radon to come into equilibrium, without appreciable reaction taking place. At the end of the 4-hr. period the bulb was placed in the oven at the temperature of the experiment.

At the end of the desired time the bulb was quickly cooled. The capillary tip was broken off under a 5 per cent potassium iodide solution. The excess bromine liberated an equivalent amount of iodine as the solution ascended into the bulb. After thorough rinsing of the bulb with distilled water, the liberated iodine was titrated with an approximately $N/50$ sodium thiosulfate solution, starch being used as an indicator. After the disappearance of the color in the starch, the solution was boiled vigorously for 2 to 3 min. It was cooled under a soda-lime tower to protect it from carbon dioxide of the air, after which the hydrogen bromide in solution was titrated with approximately $N/50$ barium hydroxide solution, using phenolphthalein as an indicator.

In standardizing the solutions the sodium thiosulfate was first checked against the pure bromine. This was accomplished by permitting an accurately weighed quantity of bromine to react with an excess of potassium iodide solution. The iodine liberated was titrated with the thiosulfate. The barium hydroxide was then checked against the pure bromine as follows: A small weighed quantity of bromine was caused to react to completion with hydrogen in a glass bulb at about 450°C. The hydrogen bromide so produced was titrated with the barium hydroxide solution. In this way both solutions relate back to the original bromine used.

In studying the effect of alpha particles upon the decomposition of hydrogen bromide, the technique employed was somewhat similar to that previously described for the synthesis. Stoichiometric quantities of bromine and hydrogen were placed in a bulb, together with radon in a

capsule. The bromine and hydrogen were brought to complete reaction by raising to a temperature of 450°C. Upon cooling the radon capsule was shattered, thus permitting the radon to act upon the pure hydrogen bromide at room temperature for as long a time as was desired.

EXPERIMENTAL RESULTS

The results of the experiments on the synthesis of hydrogen bromide are shown in tables 1 and 2. Table 2 shows the result of hydrogen bromide

TABLE 1

Effect of alpha particles upon the synthesis of hydrogen bromide

TEMPERATURE	INITIAL RADON	TIME	BULB VOLUME	RADON CONSUMED	TOTAL ION PAIRS $\times 10^{10}$	MOLECULES $\text{HBr} \times 10^{10}$	M/N TOTAL	M/N BY IONIZATION	PER CENT TOTAL REACTION	PER CENT THERMAL REACTION
°C.	millicuries	hours	cc.							
40	90.3	166.5	40.1	64.4	2.40	1.30	0.54	0.54	11.3	
100	67.4	164.5	44.6	47.8	1.70	1.33	0.78	0.66	9.8	2.4
160	96.4	119.	42.6	56.9	1.84	2.83	1.54	1.25	23.4	4.2
192	133.1	90.	40.1	65.3	2.35	4.20	1.74	1.51	37.0	5.9
202	138.4	67.	37.8	54.6	1.82	3.44	1.90	1.43	32.9	7.5
223	123.5	50.	40.4	38.6	1.35	3.77	2.80	1.37	31.5	14.7
233	115.5	50.	39.7	36.1	1.24	3.70	2.90	0.90	33.2	23.4
243	149.1	48.	39.7	45.1	1.54	4.90	3.18	0.55	42.8	37.2
243	78.7	48.	40.3	23.8	0.82	4.74	5.77	0.73	40.4	39.0
253	144.6	46.	37.5	42.2	1.42	6.63	4.67	0.42	63.5	57.0
264	112.1	11.	42.5	8.9	0.31	5.42	17.3	0.08	45.0	42.0
275	128.3	1.	37.0	0.9	0.028	1.49	53.0		14.8	14.7
303	25.0	0.5		0.1	0.003	1.46	540.0		26.0	

TABLE 2

Synthesis of hydrogen bromide

RADON	TIME	RADON CONSUMED	ION PAIRS $\times 10^{10}$	MOLECULES OF $\text{HBr} \times 10^{10}$	M/N	PER CENT REACTION	($M/N\sqrt{Rn}$)
millicuries	hours	millicuries					
56.7	145	37.6	0.595	0.718	1.21	8.8	7.41
23.3	204	18.3	0.289	0.493	1.70	5.6	7.28

synthesis at 35°C. in two cases where widely different quantities of radon were permitted to decompose. At this temperature the thermal formation is nil, thus permitting the direct effect of the alpha particles to be noted. In the last column of table 2, \sqrt{Rn} indicates radon decomposed. Since these values, when multiplied by the M/N yields, give results which are in fairly close agreement, one is led to believe that the M/N yields are proportional to the square root of the radon decomposed.

CALCULATIONS AND RESULTS

In order to calculate the number of ion pairs, N , produced during the course of an experiment, use was made of the average path method of Lind. The equation employed is as follows:

$$N = 3 \times 3.72 \times 10^{10} \cdot E \cdot 2.4 \times 10^4 \cdot \bar{p} \cdot i \cdot t (P/760)$$

in which $3 \times 3.73 \times 10^{10}$ = the number of alpha particles emitted per second by 1 curie of radon in equilibrium with radium A and radium C; E = the effective radon over the period of the experiment; 2.4×10^4 = the number of ion pairs produced per centimeter in air at S.T.P.; \bar{p} = the average path = $0.61 R$, where R is the bulb radius; i = the specific molecular ionization of the gas mixture (with 0.5 atm. each of hydrogen and bromine, a value of 2.07 for i was employed); t = the total time of the experiment in seconds. In calculating E the following equation was employed:

$$E = \frac{E_0 - E_t}{\lambda t}$$

where λ is the decay constant for radon and equals 0.0075 hr.^{-1}

The temperature coefficient of the reaction between hydrogen and bromine has already been discussed in a previous paper (8).

In table 1 the experiment performed at 40°C. indicates an M/N value of 0.54, which agrees with Lind's value obtained in his first investigation of this reaction.

In studying the M/N yield for the synthesis by alpha particles, it is found that in no case does the value exceed even 2. This appears to lead to the conclusion that the reaction is not carried on by a clustering mechanism, as was suggested earlier. The M/N values increase with rising temperature up to approximately 200°C. and then rapidly decrease. At 275°C. the total amount of reaction in the bulb with radon was practically the same as in the purely thermal run. The accompanying curve illustrates how the M/N values for ionization vary with temperature. At approximately 200°C. the thermal formation of hydrogen bromide begins to gain more and more on the ionized formation, until at 275°C. the difference is not noticeable and the M/N by synthesis appears to approach zero. In explaining the M/N yields at the lowest and highest temperatures we must realize that at 40°C. the thermal reaction is negligible and that we are dealing only with reaction produced by ions. At the higher temperature, however, especially at 275°C. and 303°C. , the ions make but a negligible contribution and thus practically the only rate being measured is the thermal one; that is, the rate of production of hydrogen bromide by thermal means is so great that its production by ionization becomes insignificant. There is no doubt that its production

by ions is still effective, but the actual measurement of hydrogen bromide formed by the ions is impracticable in the presence of such exceedingly large amounts produced thermally. These results would appear to indicate that the M/N due to ionization does not rise appreciably with increasing temperature.

In an attempt to determine the effect of alpha particles upon the decomposition of hydrogen bromide in the gas phase, two experiments were performed as detailed in table 3, at a room temperature of approximately 30°C. As is noted in column 6, a relatively high rate of decomposition resulted. Lind (5), working with the decomposition of hydrogen bromide

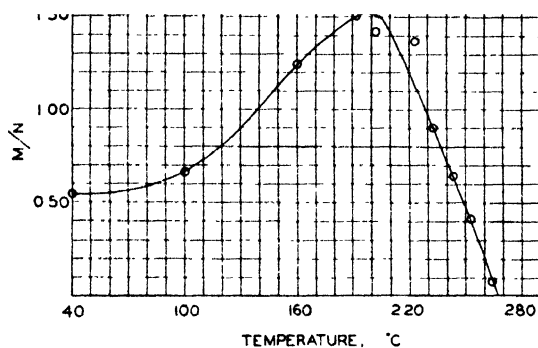


FIG. 2. Variation with temperature of the M/N values for ionization

TABLE 3

Effect of alpha particles upon the decomposition of hydrogen bromide in the gas phase

DURATION OF EXPERIMENT	INITIAL RADON	RADON CONSUMED	MOLECULES OF HBr DECOMPOSED $\times 10^{20}$	ION PAIRS $\times 10^{20}$	$-M/N$
hours	millicuries	millicuries			
48	71.50	21.60	2.10	0.76	2.76
120	66.33	39.36	3.06	0.95	3.15

in the liquid phase, found a value of -2.6 for the M/N ratio. While the values obtained for the gas phase are somewhat higher, they are still of the same order of magnitude, there being no reason why the values should be greatly different in the two cases.

As may be seen, the foregoing results indicate one great difference between the hydrogen-bromine reaction under alpha-particle radiation and the reaction brought about by thermal means. In the latter case, the reverse reaction $2\text{HBr} \rightarrow \text{H}_2 + \text{Br}_2$ is negligible, since within the possible temperature range of the investigations the equilibrium lies entirely on the side of hydrogen bromide. Similarly with the photochemical reac-

tion, hydrogen bromide is transparent to wave lengths absorbed by bromine, so that the photochemical decomposition does not come into account. However, in the case of the alpha particle effect upon hydrogen bromide, we have ionization of the gas taking place readily and, as the results of table 3 indicate, considerable decomposition takes place. Since the speed of decomposition is so great per ion pair compared with the synthesis, reverse reaction becomes sufficiently prominent to submerge the purely inhibitive effect of hydrogen bromide on the hydrogen atom. The small observed temperature coefficient may be explained by taking into account the high rate of ionic decomposition of the hydrogen bromide. This so lowers the effective rate of the forward reaction that it appears to have a much smaller temperature coefficient than the photochemical synthesis over the same temperature range, since the photochemical back reaction is not effective.

SUMMARY

The temperature coefficient of the hydrogen bromide reaction (synthesis) by alpha particles has been studied between 40° and 192°C. The average value obtained per 10°C. interval was 1.07. As the temperature rises the temperature coefficient value keeps decreasing, owing to the increasing decomposition of the hydrogen bromide formed thermally.

Owing to the fact that the M/N values were not found to exceed 2, it was concluded that the purely ionic reaction did not proceed by the clustering mechanism postulated earlier.

The M/N value for the decomposition of hydrogen bromide by alpha particles was found to be rather high compared to the M/N value for the synthesis, a value of approximately 3 being found.

Evidence was found to indicate that the M/N yields obtained at room temperature are proportional to the square root of the total radon decomposed.

The author desires to express his sincere appreciation to Dr. S. C. Lind, under whose direction this work was undertaken, and also to Dr. R. S. Livingston, who kindly assisted in the calculation and interpretation of certain of the data.

REFERENCES

- (1) BODENSTEIN AND LIND: *Z. physik. Chem.* **57**, 168 (1906).
- (2) BODENSTEIN AND LÜTKEMEYER: *Z. physik. Chem.* **114**, 208 (1925).
- (3) CHRISTIANSEN: *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.* **1**, 14 (1919).
- (4) HERZFELD: *Z. Elektrochem.* **25**, 310 (1919).
- (5) LIND: *Le radium* **8**, 289-92 (1911).
- (6) LIND: *Chemical Effects of Alpha Particles and Electrons*, revised edition, p. 93. The Chemical Catalog Co., Inc., New York (1928).
- (7) Reference 6, p. 144.
- (8) LIND AND OGG: *Z. physik. Chem., Bodenstein Festband*, pp. 801-6 (1931).
- (9) POLANYI: *Z. Elektrochem.* **26**, 49 (1920).

ACTIVITY COEFFICIENTS OF AMMONIUM CHLORIDE IN LIQUID AMMONIA AT 25°C.

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INTRODUCTION

The need for absolute values of activities of electrolytes in liquid ammonia at 25°C. has been intensified by the experimental work of recent years. Elliott and Yost (2) and Garner, Green, and Yost (3) have made electromotive force measurements which can be used for the calculation of free energies when an accurate value of the activity of ammonium chloride has been determined. The values of the standard half-cell potentials cannot be established until the activity of some electrolyte such as ammonium chloride is known.

Larsen and Hunt (5) have measured the vapor pressure of ammonia from various liquid ammonia solutions. The data obtained are useful in determining relative activities, but, since the method could not be used to determine accurate values of vapor pressure at low concentrations, accurate absolute values of activity cannot be calculated from them. Pleskov and Monosgon (7) have determined the activity coefficients of ammonium chloride and ammonium nitrate in liquid ammonia at -50°C. by measuring the electromotive force of concentration cells. Their results were obtained at a temperature much lower than is ordinarily used in the investigation of liquid ammonia solutions, and therefore do not fill the need for activity coefficients at room temperature.

This investigation was made in order to determine the activity coefficients of ammonium chloride solutions in liquid ammonia at 25°C. The experimental difficulties in using a hydrogen electrode at such a high pressure caused us to discard the possibility of using the electromotive force method. The vapor pressure method seemed to be the most applicable, since it can be used at 25°C., and since values of activities obtained by this method can be directly applied for changing the data of Larsen and Hunt (5) to absolute activities.

EXPERIMENTAL

Very few methods can be used for measuring vapor pressure to six significant figures. If an absolute method of measuring vapor pressure

were used, it would be necessary to make measurements to six significant figures in order to obtain the desired accuracy at high dilutions. For this reason, an apparatus was designed to measure the difference in vapor pressure between pure liquid ammonia and the solution of ammonium chloride in liquid ammonia. The apparatus which was used is shown in figure 1. It consisted of a tube containing pure ammonia separated from a tube containing ammonium chloride solution by means of a U-tube manometer filled with mercury. The difference in pressure between the

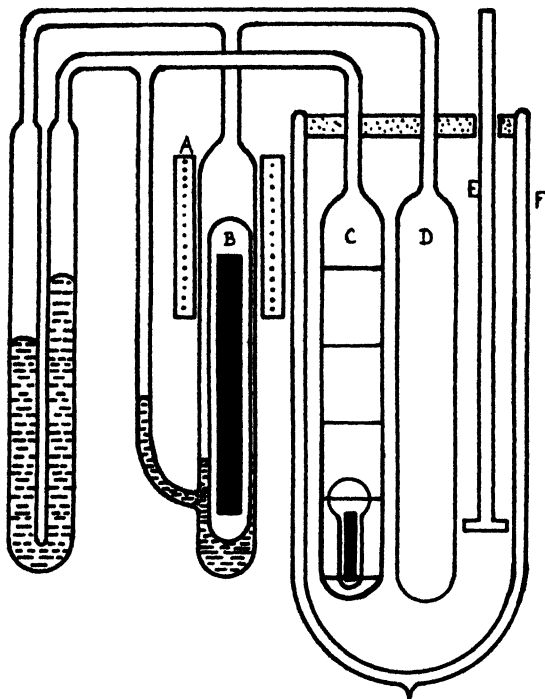


FIG. 1. Apparatus for determining the vapor pressure of dilute solutions in liquid ammonia. A, solenoid; B, plunger; C, solution; D, pure ammonia; E, stirrer; F, Dewar flask.

two tubes was found by measuring the difference in height between the two mercury levels with a Hilger traveling microscope which could be read to 0.001 mm. The two tubes were also separated by a mercury valve, which could be opened by activating the solenoid and lifting a glass-enclosed iron plunger from the mercury. This valve was opened when the tubes were filled, and also when the concentration was changed by evaporating ammonia from one tube to the other.

Ammonium chloride of analytical reagent quality was further purified by recrystallization and measured into a graduated tube, either by direct

weighing or by evaporating a known volume of a standard solution of ammonium chloride in water. This latter method was necessary in order to obtain accurately the small amount of ammonium chloride used for the dilute solutions. A glass-enclosed iron stirrer was inserted, and the tube was connected to the apparatus. The apparatus was evacuated and dried by gentle baking. Ammonia dried by sodium was distilled into a glass container, which was chilled in a dry ice-alcohol bath, and then redistilled into the apparatus. During both the first distillation and the redistillation, the apparatus was frequently partially evacuated by pumping with a Cenco pump in order to sweep out all traces of hydrogen and any other gaseous impurities. When the desired amount of ammonia had been condensed into the apparatus, the ammonia was cooled in a dry ice-alcohol bath and the apparatus was evacuated with a Cenco pump until the pressure fell to about 4 mm. of mercury. The apparatus was then sealed off and warmed to room temperature. The solution was stirred by the use of a solenoid, and the two ammonia tubes were placed in a Dewar flask containing water. The rest of the apparatus was wrapped with No. 26 gauge chromel wire spaced at about 1 cm. between turns. The whole apparatus was placed in a bath maintained at $25.000^{\circ}\text{C.} \pm 0.003^{\circ}$. The tubes in the Dewar flask were allowed to reach temperature equilibrium, which was hastened by stirring the water in the flask. The rest of the apparatus was heated slightly above the average bath temperature by passing a current through the chromel windings. This was done to prevent the condensation of ammonia in the apparatus outside the Dewar flask.

Concentrations were changed by opening the mercury valve and distilling ammonia from one tube to the other. Readings were obtained at one to four different concentrations for each filling. Three separate sets of apparatus of varying dimensions were used. The ammonia vapor was tested for gaseous impurities each time the apparatus was filled, but no impurities were found.

RESULTS

After equilibrium was reached, the difference in height between the mercury in the two arms of the U-tube was read by the traveling microscope. Molalities were calculated by using the weight of ammonium chloride placed in the tube, the volume of solution which was read from the graduations on the tube, and the density of the solution. As suitable density measurements were not found in the literature, it was necessary to measure the densities of the solutions over the range used in this investigation. These measurements were made by a modified pycnometer method, and the results are reported in table 1.

The readings of the differences in pressure between pure ammonia and

solutions of various molalities are reported in table 2 as values of $p_0 - p$, given in centimeters of mercury. These readings are corrected to 0°C. and a gravitational acceleration of 980.665. The readings were corrected for the shape of the meniscus where such correction was found to be significant.

Table 2 shows values of $1 - a_1$ at various concentrations. These values were calculated as follows:

$$1 - a_1 = 1 - \frac{f}{f_0} = \frac{f_0 - f}{f_0} \quad (1)$$

where

a_1 = activity of solvent,

f = fugacity of solvent in solution of molality m , and

f_0 = fugacity of pure solvent.

TABLE 1

Density of ammonium chloride solutions in liquid ammonia at 25°C. under pressure equal to vapor pressure of the solution

MOLALITY	DENSITY OF THE SOLUTION	APPARENT DENSITY OF AMMONIA
	grams per milliliter	grams per milliliter
0.0	0.6029	0.6029
0.0435	0.604	0.603
0.169	0.608	0.602 ₆
0.770	0.627	0.602

Values of $(p_0 - p)/p_0$ were calculated from the measured values of $p_0 - p$ divided by the value of $p_0 = 750.6$ measured by Larsen and Hunt (5). From Lewis and Randall (6) we find

$$\frac{f}{p} = 1 - \frac{\alpha p}{RT} \quad (2)$$

Values of f at various pressures were calculated by the equation of Larsen and Hunt (5), and it was found that α/RT was nearly constant over the range of pressure dealt with in our measurements. (Errors due to neglecting higher terms in equation 2 and neglecting variations in the f/p ratio amount to about 0.3 per cent.)

Placing

$$\begin{aligned} \frac{\alpha}{RT} &= K = \frac{1 - \frac{f}{p}}{p} \\ f &= p(1 - Kp) \\ \frac{f_0 - f}{f_0} &= \frac{p_0(1 - Kp_0) - p(1 - Kp)}{p_0(1 - Kp_0)} \end{aligned}$$

Expanding and factoring,

$$\frac{f_0 - f}{f_0} = \frac{p_0 - p}{p_0} \frac{1}{1 - Kp_0} - \frac{K(p_0 + p)}{1 - Kp_0}$$

Placing

$$\frac{1}{1 - Kp_0} - \frac{K(p_0 + p)}{1 - Kp_0} = A$$

$$\frac{f_0 - f}{f_0} = \frac{p_0 - p}{p_0} A$$

Evaluating A for different values of pressure, we find, for $p = 750.6, 749.6$, and 740.6 cm., that $A = 0.885, 0.885$, and 0.885 , respectively, and can be called constant over this range of pressure. This value of A and the experimental values of $(p_0 - p)/p_0$ were used in calculating the values of $(f_0 - f)/f_0$ which are listed in table 2 as values of $1 - a_1$.

The method of Randall and White (8) was used in calculating activity coefficients. Their equation, applied to a uni-univalent type of electrolyte, using liquid ammonia as the solvent, becomes

$$\ln \gamma_{\pm} = -h - 2 \int_0^{\sqrt{m}} \frac{h}{\sqrt{m}} d(\sqrt{m}) \quad (3)$$

where

$$h = 1 + \frac{58.71 \ln a_1}{2m}$$

Values of h and h/\sqrt{m} calculated from the data are given in table 2, and figure 2 shows values of h/\sqrt{m} plotted against values of \sqrt{m} . The value of the integral in equation 3 was found for values of h/\sqrt{m} taken from the curve of figure 2 up to $\sqrt{m} = 1$ by measuring the area under the curve with a planimeter. The values of γ_{\pm} obtained in this manner up to and including $m = 1$ are shown in table 3. The value of γ_{\pm} at $m = 1$ permits the evaluation of the k' given in the table of Larsen and Hunt (5), and the values of γ_{\pm} above $m = 1$ that are found in table 3 are calculated from their table of $k'\gamma$ and our value of k' , which was found to be 29.1 for ammonium chloride.

The curve of figure 2 was extrapolated to a calculated value of h/\sqrt{m} for the value of $\sqrt{m} = 0$. This calculation was made by use of the Gibbs-Duhem equation and the Debye-Hückel equation. In order to calculate this limiting value of h/\sqrt{m} , it is necessary to evaluate the constants in the Debye-Hückel equation as applied to solutes in liquid ammonia. Development of the Debye-Hückel theory for very dilute

solutions as given by Dole (1) results in the equation

$$\ln \gamma_{\pm} = -(z_+ z_-) \frac{\epsilon^3}{(DkT)^{3/2}} \sqrt{\frac{N}{1000} \sum c_i z_i^2} \quad (4)$$

TABLE 2

Data from measurements of vapor pressure of ammonium chloride solutions in liquid ammonia at 25°C.

MOLALITY	\sqrt{m}	$p_0 - p$	$1 - a_1$	h	$\frac{h}{\sqrt{m}}$
		cm. of Hg			
0.900	0.948	7.43	0.00877	0.714	0.753
0.717	0.843	6.77	0.00799	0.673	0.800
0.378	0.612	4.03	0.00475	0.633	1.03
0.190	0.435	2.74	0.00323	0.502	1.15
0.141	0.375	2.25	0.00265	0.448	1.20
0.101	0.318	1.720	0.00203	0.411	1.29
0.0575	0.240	1.065	0.00126	0.358	1.50
0.0278	0.167	0.542	0.000639	0.325	1.94
0.0098	0.099	0.213	0.000252	0.254	2.56
0.0051	0.071	0.121	0.000142	0.181	2.53

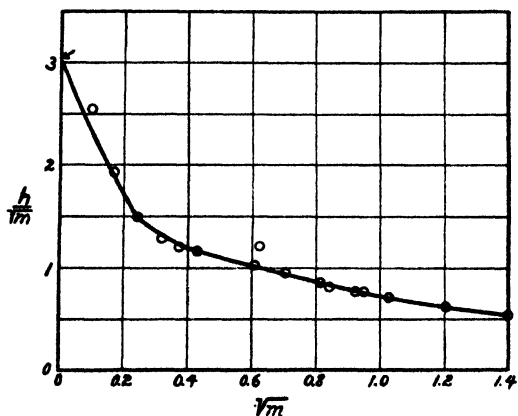


FIG. 2. Values of h/\sqrt{m} plotted against values of \sqrt{m} . Arrow indicates calculated limiting value. \oplus , data by Larsen (5); \circ , data by Ritchey.

where z_- and z_+ are the charge on anion and cation,

$\epsilon = 4.77 \times 10^{-10}$ electrostatic units,

$k = 1.37 \times 10^{-16}$ ergs per degree,

T = degrees Kelvin temperature,

$N = 6.06 \times 10^{23}$ per mole,

D = the dielectric constant of ammonia, which was found by Grubb, Chittum, and Hunt (4) to be 16.90 at 25°C., and

c = concentration in moles per liter.

Evaluating constants and changing from concentration to molality by the use of 0.603 g. per milliliter for the density of liquid ammonia at 25°C., for a uni-univalent electrolyte, equation 4 becomes

$$\ln \gamma_{\pm} = -9.06\sqrt{m} \quad (5)$$

The Gibbs-Duhem equation states

$$d \ln a_1 = -\frac{N_2}{N_1} d \ln a_2 \quad (6)$$

TABLE 3

Activity coefficients of ammonium chloride in liquid ammonia solutions of various molalities at 25°C.

MOLALITY	γ_{\pm}	\sqrt{m}	$\ln \gamma_{\pm}$
0.0025	0.653	0.050	-0.4255
0.0100	0.456	0.100	-0.784
0.0225	0.341	0.150	-1.077
0.0400	0.275	0.200	-1.290
0.160	0.139	0.400	-1.974
0.360	0.0769	0.600	-2.562
0.640	0.0488	0.800	-3.018
1.00	0.0344	1.00	-3.365
1.47	0.0254		
1.96	0.0201		
4.00	0.0111		
7.40	0.00718		
10.7	0.00604		
13.7	0.00587		
16.3	0.00608		
18.9	0.00659		
21.8	0.00732		
24.4 (saturated)	0.00822		

At molality m , N_2 divided by N_1 becomes $m/58.71$. Setting $a_2 = \gamma_{\pm}^2 m^2$, equation 6 becomes

$$d \ln a_1 = -\frac{m}{58.71} (2d \ln \gamma_{\pm} + 2d \ln m) \quad (7)$$

Differentiating equation 5,

$$d \ln \gamma_{\pm} = \frac{-9.06}{2\sqrt{m}} dm \quad (8)$$

Substituting this value for $d \ln \gamma_{\pm}$ in equation 7 and integrating,

$$\ln a_1 = \frac{2}{3} \times \frac{9.06}{58.71} m^{3/2} - \frac{2m}{58.71}$$

Multiplying both sides of the equation by $58.71/2m$ and grouping terms,

$$1 + \frac{58.71 \ln a_1}{2m} = \frac{9.06}{3} \sqrt{m}$$

The left-hand side of this equation is h by definition, and therefore

$$\frac{h}{\sqrt{m}} = 3.02 \quad (9)$$

The experimental points shown in figure 2 indicate that the value of 3.02 obtained in equation 9 is a reasonable limiting value for the extrapolation of h/\sqrt{m} . This in itself offers a partial confirmation of the validity of the Debye-Hückel theory in liquid ammonia systems. In order to test the theory further, values of $\ln \gamma_{\pm}$ and \sqrt{m} up to $\sqrt{m} = 1$ were taken from table 3 and used to plot the curve shown in figure 3.

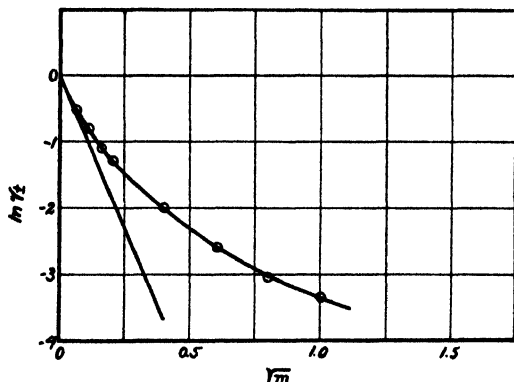
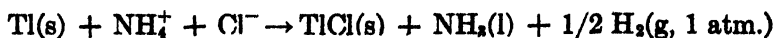


FIG. 3. Values of $\ln \gamma_{\pm}$ plotted against m

The straight line shown in figure 3 gives values of $\ln \gamma_{\pm}$ calculated from equation 5. At a molality of 0.00225, the calculated value of $\ln \gamma_{\pm}$ is in error by 6 per cent. This error increases rapidly with increasing concentration, but the agreement of calculated and actual (extrapolated) values is apparently good at concentrations of 0.001 molal and below. The fact that the Debye-Hückel theory does not hold for ammonia solutions to as high concentrations as the theory holds for water is in agreement with the great difference of dielectric constant between ammonia and water.

CALCULATION OF ELECTRODE POTENTIALS

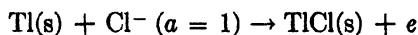
Elliott and Yost (2) have measured the potential of the cell in which the reaction is



using electrodes of thallium amalgam and hydrogen gas. Assuming that $F = 0$ for the reaction



as is comparable to the assumption made for aqueous solutions, the molal electrode potential for the half-cell



could be calculated from their measurements and values of activity coefficients. However, experimental difficulties were such that their values of potential are uncertain and a better value of potential probably can be obtained by calculation from free energies of formation. Garner, Green, and Yost (3) made this calculation, using the following values for standard free energies of formation at 25°C.; $\text{NH}_4\text{Cl}(\text{s}) = -47,810$ cal., $\text{TlCl}(\text{s}) = -44,164$ cal., $\text{NH}_3(\text{l}) = -2620$ cal. It is also necessary to know the free energy change for the reaction



TABLE 4

Standard electrode potentials in liquid ammonia at 25°C.

HALF-CELL REACTION	$E_{298.1}^0$
	<i>volts</i>
$\text{Tl}(\text{s}) + \text{Cl}^- \rightarrow \text{TlCl}(\text{s}) + e$	+0.0371
$\text{Zn}(\text{s}) + 2\text{Cl}^- + 6\text{NH}_3(\text{l}) \rightarrow \text{ZnCl}_2 \cdot 6\text{NH}_3(\text{s}) + 2e$	+0.8664
$\text{Cd}(\text{s}) + 2\text{Cl}^- + 6\text{NH}_3(\text{l}) \rightarrow \text{CdCl}_2 \cdot 6\text{NH}_3(\text{s}) + 2e$	+0.5059

The value obtained for this reaction by Garner, Green, and Yost (3) is inaccurate, because they calculated values of activity coefficients from insufficient data. Using values of activity coefficients from table 3 for calculation of the free energy change in the preceding reaction,

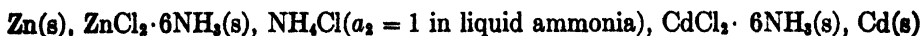
$$\begin{aligned} \Delta F &= -2.3RT \log \frac{1}{\text{NH}_4\text{Cl}(\text{s})} = -1364.5 \log \frac{1}{\text{NH}_4\text{Cl}(\text{satd. soln.})} \\ &= -1364.5 \log \frac{1}{(24.4 \times 0.00822)^2} = 1903 \text{ cal.} \end{aligned}$$

Adding these values of free energies, for the thallium-thallos chloride half-cell,

$$\Delta F_{298.1}^0 = -877 \text{ cal.}$$

$$E_{298.1}^0 = +0.0371 \text{ volts}$$

Garner, Green, and Yost (3) found $E_{298.1}^0 = 0.3605$ volt for the cell



Elliott and Yost (2) found $E_{298.1}^0 = 0.8293$ volt for the cell

$\text{Zn(s)}, \text{ZnCl}_2 \cdot 6\text{NH}_3(\text{s}), \text{NH}_4\text{Cl}(a_2 = 1 \text{ in liquid ammonia}), \text{TlCl(s)}, \text{Tl(s)}$

Combining the measured values of $E_{298.1}^0$ for these cells with the calculated value of $E_{298.1}^0$ for the thallium-thallic chloride half-cell gave the values for the half-cells reported in table 4.

SUMMARY

1. The vapor pressure difference between solutions of ammonium chloride in liquid ammonia and pure liquid ammonia has been determined for solutions ranging from 0.0051 molal to 0.900 molal.

2. Activity coefficients for ammonium chloride in liquid ammonia at various molalities have been calculated from the vapor pressure data, using the method of Randall and White.

3. The Debye-Hückel theory as applied to activity coefficients of ammonium chloride in liquid ammonia has been tested and found to hold only at very low molalities.

4. Standard electrode potentials have been calculated from the free energies of formation, the potential measurements of Yost and coworkers, and our measured values of activity coefficients.

REFERENCES

- (1) DOLE: Experimental and Theoretical Electrochemistry. McGraw-Hill Book Company, New York (1935).
- (2) ELLIOTT AND YOST: J. Am. Chem. Soc. **56**, 1057 (1934).
- (3) GARNER, GREEN, AND YOST: J. Am. Chem. Soc. **57**, 2055 (1935).
- (4) GRUBB, CHITTUM, AND HUNT: J. Am. Chem. Soc. **58**, 776 (1936).
- (5) LARSEN AND HUNT: J. Phys. Chem. **38**, 801 (1934); **39**, 877 (1935).
- (6) LEWIS AND RANDALL: Thermodynamics. McGraw-Hill Book Company, New York (1923).
- (7) PLESKOV AND MONOSGON: J. Phys. Chem. (U.S.S.R.) **6**, 513 (1935).
- (8) RANDALL AND WHITE: J. Am. Chem. Soc. **48**, 2514 (1926).

MOLECULAR FORCES AND SOLVENT POWER¹

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The object of this investigation was to correlate the phenomenon of solubility with the physical properties of the solute and solvent. Chlorides, bromides, and iodides of potassium and sodium were studied in an homologous series of aliphatic alcohols. The data in the literature show large discrepancies for these solubilities, and data are available only for a part of the salts.

EXPERIMENTAL

The method described by Seidell (7) and Reilly (6) for determining solubilities, together with their precautions for reliable work, were used generally. In our determinations saturated solutions were obtained by agitation of the salt-alcohol mixture, in a sealed bottle suspended in a water thermostat whose temperature was controlled to $25^{\circ}\text{C.} \pm 0.02^{\circ}$. The saturated solution, after settling, was forced through a sintered-glass filter into a density tube or weighing bottle for the analysis. All reagents were transferred from one container to another without exposure to the atmosphere. The density tubes had a capacity of about 30 ml. They were of the capillary stem type and were filled with a platinum tube. The analytical equipment was all calibrated against apparatus certified by the National Bureau of Standards. The solvent was removed carefully from the weighed sample by overhead electrical heating. The warm residue was dried completely with a stream of washed dry air. About 100 ml. of the solutions which were rich in solute was used for the analysis and about 1 liter of the other solutions. When the amount of residue became so small that its weight could not be determined gravimetrically with accuracy, the halides were determined by Volhard's titrimetric method, as modified by V. Rothmund and A. Burgstaller (10).

Methanol was dried by refluxing with sodium or a large excess of Drierite (anhydrous calcium sulfate) (4) for several hours before distilling off the alcohol. Absolute ethanol (8) was obtained by using barium oxide for preliminary dehydration and metallic calcium turnings for the removal

¹ Presented at the Ninety-fifth Meeting of the American Chemical Society, held at Dallas, Texas, April, 1938.

TABLE 1

Solubilities of inorganic salts in aliphatic alcohols at 25°C. and densities of the saturated solutions

SOLVENT	NaCl		NaBr		NaI	
	Solubility*	Density†	Solubility	Density	Solubility	Density
Water.....	36.05		93.5		184.5	
Methanol.....	1.401	0.7977	17.36	0.9073	80.53	1.2615
Ethanol.....	0.0649	0.7857	2.406	0.8019	43.320	1.0466
1-Propanol.....	0.0124	0.8000	0.4562	0.8026	27.65	0.9699
1-Butanol.....	0.0050	0.8058	0.246	0.8075	21.60	0.9397
2-Propanol.....	0.0027	0.7809	0.1313	0.7818	26.320	0.9422
2-Methyl-1-propanol.....	0.0020	0.7980	0.0951	0.7986	17.68	0.9085
1-Pentanol.....	0.00177	0.8099	0.1103	0.8106	16.31	0.9127
2-Butanol.....	0.00047	0.8022	0.0341	0.8025	15.02	0.8968
	KCl		KBr		KI	
	Solubility	Density	Solubility	Density	Solubility	Density
Water.....	39.9		67.75		148.3	
Methanol.....	0.5391	0.7907	2.11	0.8025	17.04	0.8982
Ethanol.....	0.0294	0.7852	0.1350	0.7861	1.88	0.7977
1-Propanol.....	0.0061	0.7994	0.0314	0.8010	0.444	0.8035
1-Butanol.....	0.0030	0.8058	0.0132	0.8058	0.201	0.8071
2-Propanol.....	0.0023	0.7809	0.0110	0.7810	0.177	0.7821
2-Methyl-1-propanol.....	0.0020	0.7980	0.0076	0.7980	0.0955	0.7986
1-Pentanol.....	0.0022	0.8096	0.0048	0.8096	0.0894	0.8112
2-Butanol.....	0.00084	0.8022	0.0044	0.8022	0.0582	0.8026

* The solubility is given in grams of salt per 100 grams of solvent.

† The density is given in grams per milliliter.

TABLE 2

Physical constants of solvents at 25°C.

SOLVENT	MOLECULAR WEIGHT	PARACHOR $= \frac{M\gamma^{\frac{1}{2}}}{D-d}$	DENSITY	SURFACE TENSION	DIELECTRIC CONSTANT
			grams per milliliter	dynes per centimeter	
Water.....	18	52.7	0.9977	72	78
Methanol.....	32.03	88.4	0.7866	22.18	30.2
Ethanol.....	46.05	126.8	0.7851	21.85	24.14
1-Propanol.....	60.06	164.4	0.8001	23.4	20.08
1-Butanol.....	74.08	203.9	0.8057	24.2	16.98
2-Propanol.....	60.06	165.2	0.7810	21.3	18.55
2-Methyl-1-propanol.....	74.08	202.0	0.7979	22.4	17.32
1-Pentanol.....	88.10	240.5	0.8095	23.75	13.77
2-Butanol.....	74.08	200.4	0.8025	22.2	15.77

of the last traces of moisture. All of the other alcohols were fractionated in a 6-ft. Penn State type of fractionating column (14). The constant-boiling fraction was refluxed with calcium, and only the middle fraction of the distillate was saved. Calcium forms a blue suspension in the higher alcohols during the refluxing process.

The final criterion of purity of the alcohols was their density. Only those liquids were used as solvents whose densities agreed with values given in the International Critical Tables to 0.1 or 0.2 mg. per milliliter. Our densities are in agreement with those of Brunel, Crenshaw, and Tobin (2). We offer a new value for the density of 1-pentanol at 25°C. of 0.8095 g. per milliliter. c.p. salts were recrystallized three times and dried for a long period of time at 115°C. Saturated solutions were obtained, since (1) excess salt was present at the end of several days shaking, (2) density values for the same combination checked for different determinations, and (3) the saturation point was approached from both sides of the equilibrium condition at 25°C. The solubilities of the salts and the densities of the saturated solutions are recorded in table 1. It should be noted that the very soluble salt, sodium iodide, does not follow the same order of solubility in 2-propanol that the less soluble salts do.

The dielectric constants given in the literature for some of the alcohols are unreliable, therefore these constants were determined. The heterodyne beat method with a frequency of about three thousand cycles per second was used. Our value for the dielectric constant of ethanol checks that obtained by Wyman (15), namely, 24.28. Table 2 contains the dielectric constant data as well as the parachors of the solvents.

DISCUSSION OF RESULTS

The phenomenon of solubility is a function of the attractive forces between the ions and molecules in the solution. Figure 1 shows the relationship between the solubility of the salt and the parachor of the solvent. The normal alcohols give a smooth curve, which may be extrapolated to the parachor of water. The extrapolated value is slightly higher than the actual solubility of the salt in water. The dotted lines show the solubility of a very soluble salt, sodium iodide, and a sparingly soluble salt, potassium chloride, in 2-propanol, 2-butanol, and 2-methyl-1-propanol. The other salts in these three alcohols give similar curves with respect to the curve for the normal alcohols. Sugden's parachor (9) is defined by the expression,

$$P = M\gamma^{1/4}/(D - d)$$

where M is the molecular weight of the liquid, D its density, γ its surface tension, and d is the density of the vapor, all measured at the same temperature. This physical property of the solvent does not give a marked

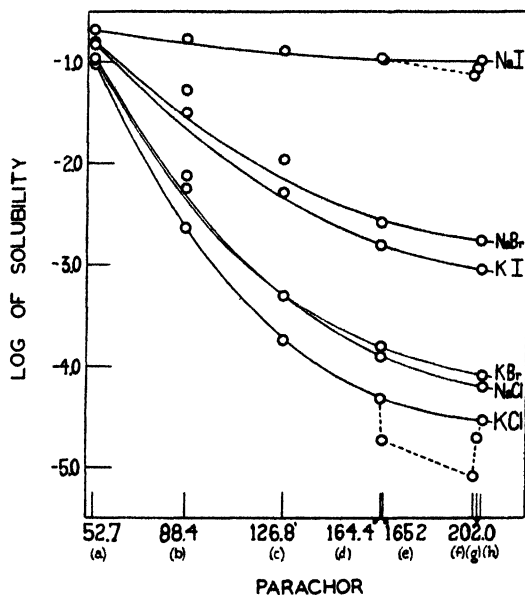


FIG. 1. The relationship between solvent power and parachor of solvent. Plot of parachor against logarithm of solubility expressed in moles of solute per mole of solvent. a, water; b, methanol; c, ethanol; d, 1-propanol; e, 2-propanol; f, 2-butanol; g, 2-methyl-1-propanol; h, 1-butanol.

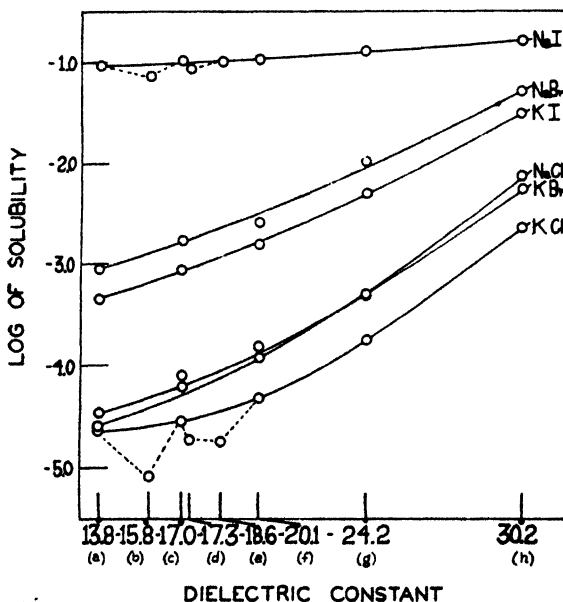


FIG. 2. The relationship between solvent power and dielectric constant of solvent. Plot of dielectric constant against logarithm of solubility expressed in moles of solute per mole of solvent. a, 1-pentanol; b, 2-butanol; c, 1-butanol; d, 2-methyl-1-propanol; e, 2-propanol; f, 1-propanol; g, ethanol; h, methanol.

distinction between isomers, and therefore cannot give us a quantitative relationship between solvent power and molecular forces.

Figure 2 shows the relationship between solubility and the dielectric constants of the alcohols. The data for the normal alcohols give a smooth curve, but on extrapolating it to the dielectric constant of water the correct solubility value is not obtained. Plotting the parachors of the alcohols against the logarithms of their dielectric constants gives a straight line, which will extrapolate to give a value for the dielectric constant of water

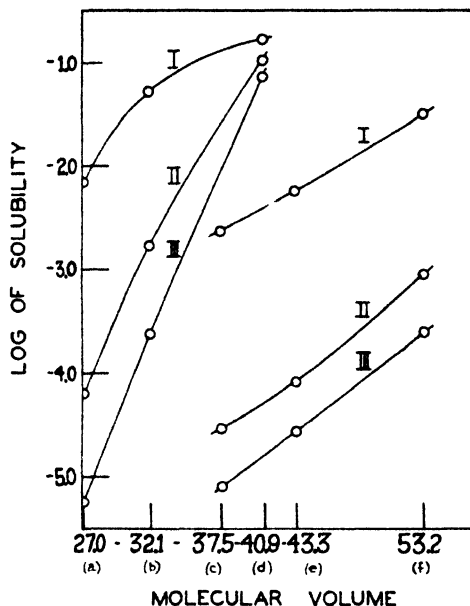


FIG. 3. The relationship between solvent power and molecular volume of solute. Plot of molecular volume of solute against logarithm of solubility expressed in moles of solute per mole of solvent. a, sodium chloride; b, sodium bromide; c, potassium chloride; d, sodium iodide; e, potassium bromide; f, potassium iodide. Curves I, methanol; curves II, 1-butanol; curves III, 2-butanol.

only one-half its commonly accepted value. If one uses this smaller value of the dielectric constant, then the solubilities of the salts in water will fit on the curves of figure 2. The dotted lines indicate the same relationship for the secondary and iso alcohols. Walden (12) made the statement that the linear solubility of a given salt in different solvents is proportional to the dielectric constant of the solvent. Such is the case for the normal alcohols but not for their iso or secondary isomers. Fredenhagen (2) has already shown that solvent power and dielectric constant do not run parallel.

Figure 3 gives the relationship between the solubility in methanol,

1-butanol, and 2-butanol and the molecular volumes of the solutes. Those for the other alcohols have been omitted for the sake of clarity but are similar in nature; the values for ethanol and 1-propanol are intermediate between those for methanol and 1-butanol. In like manner the values for 2-propanol and 2-methyl-1-propanol are between those for 1-butanol and 2-butanol. The curves suggest a linear increase in the solubility with increasing molecular volume for the less soluble salts.

Born's equation

$$\log S_1/S_2 = (0.4343e^2/2rkT)(1/D_2 - 1/D_1)$$

where e is the charge on the electron, k is Boltzmann's constant, r is the radius of the molecule, and S is the solubility in a solvent of dielectric constant D , does not fit our data. We are in need of data on the internal pressure of liquids in order to predict their solvent power.

Water enjoys the ability to form hydrogen bonds to a greater extent than any of the alcohols and therefore is a more highly associated liquid and a better solvent. If a liquid that can form hydrogen bonds is a good solvent, then we would predict that 2-butanol would be the poorest solvent of our series. Our data show this to be true. We think that it is for this reason that 2-propanol, which has a higher dielectric constant and lower parachor, is a poorer solvent than 1-butanol.

Solubilities of the salts in the normal alcohols decrease regularly with increase in molecular weight, parachor, molecular volume, boiling point, and heat of vaporization of the solvent, and increase regularly with an increase in the dielectric constant and internal pressure of the dissolving medium. With the exception of ethanol, a regular decrease in solubility occurs with an increase in density of the solvent. In all cases the normal alcohols were better solvents than the corresponding iso alcohols. The latter, in turn, are better solvents than the secondary isomers.

The sodium salts are more soluble than the corresponding potassium salts. For a given series the solubility increases in the order chloride, bromide, and iodide. Those properties of the solute which may be correlated with greater solubility are the following: large molecular volume, large molecular weight, high density, low melting point, low heat of vaporization, and low atomic weight of the metallic element. These factors emphasize the concept that the solution forces of the solvent are directly dependent upon the mass and the area over which its attractive tendencies can be exerted.

The relationships that we have pointed out hold for the data in the literature except for incredible cases such as lithium and calcium perchlorates, which are reported (13) to be much more soluble in methanol than in water.

SUMMARY

The solubility values for the iodides, bromides, and chlorides of sodium and potassium in the solvents methanol, ethanol, 1-propanol, 1-butanol, 2-propanol, 2-methyl-1-propanol, 1-pentanol, and 2-butanol have been accurately determined at 25°C.

The dielectric constants of the alcohols were determined by the heterodyne beat method.

The phenomenon of solubility was correlated in a qualitative manner with the physical constants of solvent and solute.

REFERENCES

- (1) BORN: *Z. Physik* **1**, 45 (1920).
- (2) BRUNEL, CRENSHAW, AND TOBIN: *J. Am. Chem. Soc.* **43**, 574-6 (1921).
- (3) FREDENHAGEN: *Z. Elektrochem.* **37**, 257-71 (1931).
- (4) HAMMOND AND WITHROW: *Ind. Eng. Chem.* **25**, 1112-15 (1933).
- (5) International Critical Tables, Vol. IV, pp. 447-51. McGraw-Hill Book Co., New York (1928).
- (6) REILLY: *Physico-Chemical Methods*, pp. 415-19. D. Van Nostrand Co., New York (1932).
- (7) SEIDEL: *Solubilities of Inorganic and Organic Compounds*, pp. 757-84. D. Van Nostrand Co., New York (1919).
- (8) SMITH, G. FREDERICK: *Ind. Eng. Chem., Anal. Ed.* **1**, 72-4 (1929).
- (9) SUGDEN: *J. Chem. Soc.* **125**, 1177 (1924).
- (10) TREADWELL AND HALL: *Analytical Chemistry*, Vol. II, pp. 654-6. John Wiley and Sons, Inc., New York (1932).
- (11) TURNER AND BISSETT: *J. Chem. Soc.* **103**, 1904 (1913).
- (12) WALDEN, P.: *Z. physik. Chem.* **55**, 683-720 (1906).
- (13) WILLARD AND SMITH: *J. Am. Chem. Soc.* **45**, 286 (1923).
- (14) WILSON, PARKER, AND LAUGHLIN: *J. Am. Chem. Soc.* **55**, 2795 (1933).
- (15) WYMAN, J.: *J. Am. Chem. Soc.* **53**, 3292-301 (1931).

TOTAL AND PARTIAL PRESSURES OF BINARY SOLUTIONS OF THE BUTYL ALCOHOLS IN BENZENE AT 25°C.¹

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The differential static method of measuring vapor pressures, as devised by Parks and Schwenck (8), has been modified recently by Olsen and Washburn (6) and has been applied by them to the investigation of the system benzene-isopropyl alcohol. The latter authors claim an accuracy to within 2 to 3 per cent for their method when their results are compared with recognized recorded values.

In this laboratory it was decided to employ the method in modified form. The systems chosen were the binary solutions of the four butyl alcohols in benzene. It was hoped that the results would yield information concerning the effect of the branching of the chain or of the position of the hydroxyl group upon the degree of deviation from ideality of these solutions of the non-polar-polar type.

EXPERIMENTAL

The method in essentials was that of Olsen and Washburn (6) and consisted of the comparison of the vapor pressure of the pure alcohol with the *total* pressure of a solution of that alcohol in benzene. This comparison was effected by placing the pure alcohol in one arm of a glass manometer containing mercury and the solution in the other arm, also over mercury. The technique was essentially that of Olsen and Washburn; certain refinements were introduced and will be described later.

The *partial* pressures of the constituents of the solutions were determined by passing dry, carbon dioxide-free air through bubblers containing the solutions, condensing the vaporized constituents at about $-65^{\circ}\text{C}.$, and analyzing the condensate.

Purification of materials

Benzene of reagent grade was refluxed with mercuric acetate and then distilled onto freshly pressed sodium wire. It was allowed to remain in

¹ Contribution No. 137 from the Department of Chemistry and Chemical Engineering of the University of Texas.

contact with the sodium for 36 hr.; after distilling from the sodium-sodium oxide residue, the benzene was carefully fractionated twice through an efficient column. The final product, roughly 50 per cent of the original sample, boiled at 79.6°C. at 746 mm. It melted at 5.5°C. and had at 25°C. a refractive index of 1.4980 and a density of 0.8732 g. per cubic centimeter.

The butyl alcohols were products of high quality obtained from the Eastman Company. They were purified by a preliminary refluxing with lime, followed by distillation onto calcium metal turnings. After a 12-hr. contact with the metal, the alcohols were distilled slowly from the calcium alcoholate residue and fractionally distilled thrice through a long insulated column of the indented type. The final product represented from 50 to 60 per cent of the original sample. The observed physical constants of these purified samples are presented in table 1.

TABLE 1
Physical constants of the butyl alcohols

BUTYL ALCOHOL	BOILING POINT		n_D^{25}		D_4^{25}		REFER- ENCES
	Observed	Literature	Observed	Literature	Observed	Literature	
	°C.	°C.			grams per cubic centimeter		
Normal. . . .	117.3 (746 mm.)	117.71 (760 mm.)	1.3974	1.3974	0.8057	0.8057	(2)
Iso.	107.6 (749 mm.)	107.89 (760 mm.)	1.3936	1.3939	0.7982	0.7976	(2, 1)
Secondary . .	99.2 (750 mm.)	99.53 (760 mm.)	1.3946	1.3950	0.8022	0.8023	(1)
Tertiary* . .	82.3 (752 mm.)	82.55	1.3845		0.7804	0.7806	(3)

* Observed melting point, 25.4°C.; literature value, 25.50°C. (7).

Preparation and analysis of solutions

All solutions were prepared by weight, using weight burets. Weighings were made directly into volumetric flasks equipped with special seals to exclude moisture. For each alcohol there were prepared five solutions in benzene; the *exact* concentrations were approximately 20, 35, 50, 65, and 80 mole per cent alcohol. In addition, approximately 10 mole per cent solutions of the secondary and the tertiary alcohols were prepared.

The refractive indices at 25°C. $\pm 0.1^\circ$ were determined for these solutions by means of an Abbé refractometer, using daylight as the light source. The following relations represent the dependence of the index of refraction on the mole fraction, x , of the alcohol (in the alcohol-benzene solution):

<i>n</i> -Butyl alcohol.	$n = 1.4980 - 0.1122x + 0.0116x^2$
Isobutyl alcohol.	$n = 1.4980 - 0.1184x + 0.0140x^2$
Secondary butyl alcohol.	$n = 1.4980 - 0.1214x + 0.0180x^2$
Tertiary butyl alcohol.	$n = 1.4980 - 0.1374x + 0.0240x^2$

These relations reproduce the experimentally determined values to better than 1 part in 5000. In the determination of the composition of the condensate resulting in the air-bubbling procedure of determining the partial pressures, a determination of the index yielded the molar composition immediately.

The densities of the alcohol-benzene solutions were also determined at $25^{\circ}\text{C.} \pm 0.05^{\circ}$ by means of a Weld precision specific gravity bottle. The following relations were obtained, the densities in grams per cubic centimeter being reported as functions of the mole fraction, x , of the alcohol in the benzene solution:

<i>n</i> -Butyl alcohol	$d = 0.8732 - 0.0773x + 0.0098x^2$
Isobutyl alcohol	$d = 0.8732 - 0.08917x + 0.01417x^2$
Secondary butyl alcohol	$d = 0.8732 - 0.0918x + 0.0208x^2$
Tertiary butyl alcohol	$d = 0.8732 - 0.1240x + 0.0312x^2$

These densities were necessary to make the proper corrections for the height of the alcohol-benzene solutions above the mercury in the arm of the manometer in which total pressures are determined.

The apparatus

All measurements of vapor pressure were made in a water thermostat with glass windows. The temperature was kept at $25^{\circ}\text{C.} \pm 0.05^{\circ}$ by means of a mercury column actuating a sensitive relay. All temperatures were determined by means of a long mercury thermometer of limited range calibrated by the National Bureau of Standards.

Total pressures were determined by means of the manometer described by Olsen and Washburn (6), the arms being about 40 cm. long and ending in glass-mercury seals. All readings were made with a cathetometer reading to 0.1 mm. The pure alcohols used in one arm of the manometer had the following vapor pressures at 25°C. : *n*-butyl, 6.44 mm. (4); isobutyl, 12.6 mm.; secondary butyl, 18.4 mm.; and tertiary butyl, 42.0 mm. (7). The values for the isobutyl and secondary butyl alcohols were determined in this laboratory, no values being available in the literature.

The aerator used in the partial pressure determinations was essentially that of Olsen and Washburn (6) and was maintained in a constant-temperature bath at $25^{\circ}\text{C.} \pm 0.05^{\circ}$. The condenser was kept in a dry ice-acetone bath during a run, assuring complete condensation of the vapors. At least 2 cc. of condensate was collected during each run; the composition of the condensate was read from a large-scale plot of the index of refraction *versus* the mole fraction of alcohol.

Accuracy of the method

An examination of the Olsen and Washburn total pressure method reveals that errors are due to (a) impurities in the substances investigated,

TABLE 2
Total pressures at 25°C. of benzene-butyl alcohol solutions

n-BUTYL ALCOHOL		ISOBUTYL ALCOHOL		SECONDARY BUTYL ALCOHOL		TERTIARY BUTYL ALCOHOL	
<i>z</i>	<i>p</i>	<i>z</i>	<i>p</i>	<i>z</i>	<i>p</i>	<i>z</i>	<i>p</i>
0.000	94.4(5)			0.095	96.4	0.100	104.7
0.200	89.4	0.202	93.2	0.197	95.1	0.198	106.5
0.322	84.9	0.343	89.3	0.353	91.0	0.351	104.3
0.500	77.8	0.498	83.7	0.500	85.4	0.499	100.2
0.650	67.3	0.640	75.3	0.646	76.9	0.652	92.8
0.803	50.5	0.805	56.8	0.797	60.7	0.802	80.5
1.000	6.4(4)	1.000	12.6	1.000	18.4	1.000	42.0(7)

TABLE 3
Partial pressures at 25°C. of benzene-butyl alcohol solutions

BUTYL ALCOHOL	MOLE FRACTION OF ALCOHOL IN LIQUID	n_D^{20} OF CONDENSATE	MOLE FRACTION OF ALCOHOL IN VAPOR	PARTIAL PRESSURE	
				Alcohol	Benzene
Normal	0.197	1.4927	0.045	4.0	85.3
	0.313	1.4910	0.059	5.1	80.7
	0.500	1.4897	0.070	5.5	72.4
	0.650	1.4886	0.081	5.5	61.9
	0.798	1.4850	0.113	5.8	45.8
Iso	0.202	1.4892	0.072	6.7	86.4
	0.343	1.4874	0.087	7.8	81.5
	0.498	1.4848	0.099	8.3	75.4
	0.604	1.4827	0.128	9.6	65.7
	0.805	1.4759	0.187	10.6	46.2
Secondary	0.197	1.4845	0.112	10.7	84.5
	0.353	1.4821	0.133	12.1	78.9
	0.500	1.4796	0.150	12.8	72.6
	0.646	1.4756	0.185	14.2	62.7
	0.797	1.4669	0.262	15.9	44.8
Tertiary	0.100	1.4798	0.130	13.6	91.1
	0.198	1.4712	0.196	20.9	85.7
	0.351	1.4650	0.245	25.6	78.7
	0.499	1.4593	0.291	29.2	71.0
	0.652	1.4520	0.352	32.7	60.1
	0.802	1.4400	0.455	36.6	43.9

(b) errors made in making up the solutions, (c) errors in the temperature control, (d) errors in the cathetometer readings, and (e) the presence of a small bubble of permanent gas in the manometer. In the present investi-

gation the over-all accuracy of the method is believed to be within ± 1 per cent. This was checked by measuring the vapor pressure of benzene of highest purity; the measured value and the "best" value recorded in the literature agree to within 1 per cent.

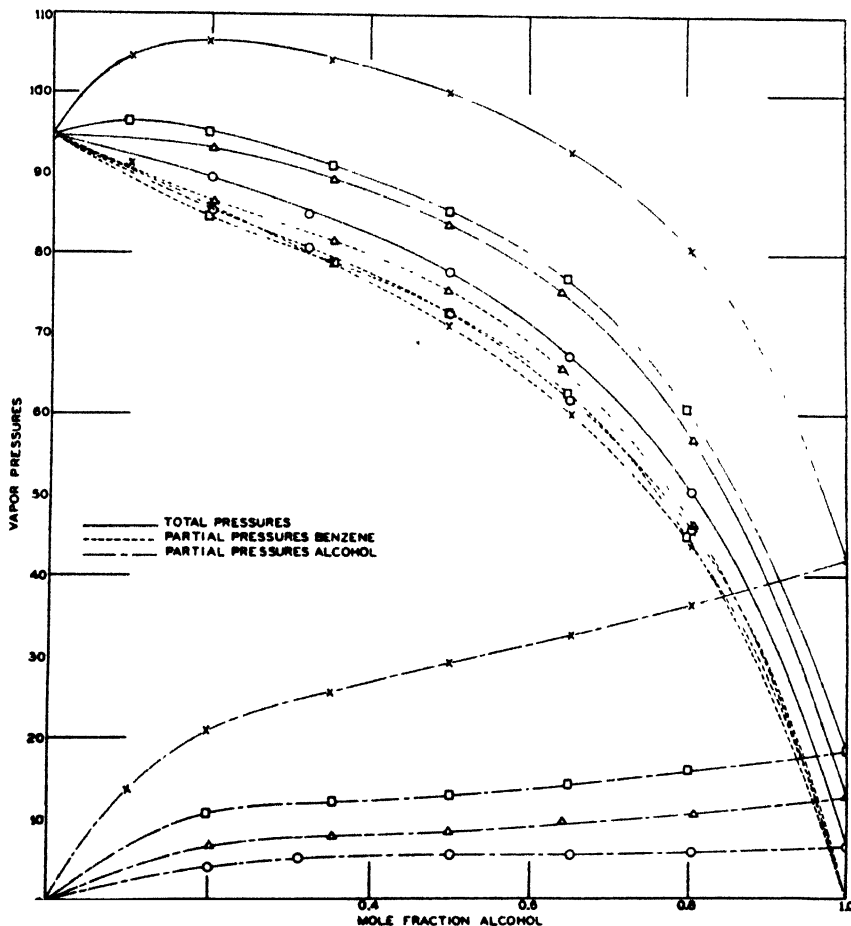


FIG. 1. Partial and total pressures (in millimeters) at 25°C. of benzene-butyl alcohol solutions. O, *n*-butyl alcohol-benzene solutions; Δ, isobutyl alcohol-benzene solutions; □, secondary butyl alcohol-benzene solutions; X, tertiary butyl alcohol-benzene solutions.

THE DATA OBTAINED

The total and partial vapor pressures are presented in tables 2 and 3 and graphically in figure 1. Pressures are given in millimeters of mercury (1/760 of standard atmosphere); the mole fraction of the alcohol is designated by x .

DISCUSSION OF RESULTS

An inspection of the curves of the figure reveals that there is a marked deviation from ideality (i.e., Raoult's law) in each of the four cases studied. This deviation was to be expected, since these solutions are composed of non-polar and polar (or semi-polar) constituents. Most striking is the comparison of the structural effects of the isomers on ideality in solution; the figure shows that vapor pressures of solutions of *n*-butyl alcohol in benzene most nearly approximate the ideal, while those of tertiary butyl alcohol in the same solvent vary most. This may indicate that a substitution of the hydrogen of the carbinol carbon by an alkyl group causes an increased deviation from ideality; i.e., that the polarity of the alcohol increases as the hydrogens of the carbinol carbon are substituted by alkyls, thereby increasing effects due to differences in the polarity of the constituents. This latter observation is in accord with accepted electronic structures of these alcohols.

SUMMARY

1. Total pressures of binary solutions of the four butyl alcohols in benzene have been measured with an accuracy within 1 per cent.
2. Partial pressures of these solutions have been determined with an accuracy better than 1 per cent.
3. The observed data are presented graphically. Such plots show a marked difference in the degree of deviation from Raoult's law for the four isomeric alcohols. An increasing polarity with change in structure of the alcohols in mixtures with the non-polar substance benzene seems to account for the increase in deviation.

REFERENCES

- (1) BRUNEL: J. Am. Chem. Soc. **45**, 1334 (1923).
- (2) BRUNEL, CRENSHAW, AND TOBEN: J. Am. Chem. Soc. **43**, 561 (1921).
- (3) DOROSHEVSKI: J. Russ. Phys. Chem. Soc. **43**, 66 (1911); Chem. Abstracts **6**, 10 (1912).
- (4) International Critical Tables, Vol. III, p. 219. McGraw-Hill Book Co., New York (1928).
- (5) Reference 4, p. 221.
- (6) OLSEN AND WASHBURN: J. Phys. Chem. **41**, 457 (1937).
- (7) PARKS AND BARTON: J. Am. Chem. Soc. **50**, 24 (1928).
- (8) PARKS AND SCHWENCK: J. Phys. Chem. **28**, 720 (1924).

CALCULATION OF HEAT OF REACTION FROM EQUILIBRIUM CONSTANTS AT TWO TEMPERATURES; SOME NEW HEATS OF IONIZATION OF ORGANIC ACIDS

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THEORETICAL

A recently published note (2) pointed out the fact that van't Hoff's isochor

$$d(\ln K) = \frac{\Delta H}{RT^2} dT \quad (1)$$

which relates equilibrium constant, heat of reaction, and absolute temperature, can be combined with the equation for the linear variation of heat of reaction with temperature,

$$\Delta H = a + bT \quad (2)$$

and integrated between limits to give¹

$$\frac{RT_1T_2 \ln K_2/K_1}{T_2 - T_1} = a + b \frac{T_1T_2}{T_2 - T_1} \ln T_2/T_1 \quad (3)$$

It was also pointed out that if a temperature, T_0 , is defined by the equation

$$T_0 = \frac{T_1T_2}{T_2 - T_1} \ln \frac{T_2}{T_1} \quad (4)$$

the right-hand member of equation 3 is ΔH_0 , the value of ΔH at T_0 , and

$$\Delta H_0 = R \frac{T_1T_2}{T_2 - T_1} \ln \frac{K_2}{K_1} \quad (5)$$

It was shown that when ΔH is a linear function of temperature equation 5 can be used to calculate ΔH from two values of K and their corresponding temperatures, and that a knowledge of the values of a and b is not required.

¹ An error in sign was observed in the original equation.

The present paper will undertake to show that ΔH may be approximated very closely by a similar procedure, even though it varies as a general equation of higher degree where the coefficients of the temperature terms are constants:

$$\Delta H = a + bT + cT^2 + dT^3 + eT^4 \quad (6)$$

Substitution of equation 6 in equation 1 and integration between the limits K_1 , K_2 and T_1 , T_2 gives

$$R \ln \frac{K_2}{K_1} = a \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + b \ln \frac{T_2}{T_1} + c(T_2 - T_1) + d \frac{(T_2^2 - T_1^2)}{2} + e \frac{(T_2^3 - T_1^3)}{3} \quad (7)$$

and multiplication by $\frac{T_1 T_2}{T_2 - T_1}$ and simplification of terms gives

$$\frac{RT_1 T_2}{T_2 - T_1} \ln \frac{K_2}{K_1} = a + b \frac{T_1 T_2}{T_2 - T_1} \ln \frac{T_2}{T_1} + c T_1 T_2 + d \frac{(T_2 + T_1)}{2} T_1 T_2 + e \frac{(T_2^2 + T_1 T_2 + T_1^2)}{3} T_1 T_2 \quad (8)$$

If

$$T_0 = \frac{T_1 T_2}{T_2 - T_1} \ln \frac{T_2}{T_1}$$

and if T_1 and T_2 are near room temperature and are not taken over too wide a temperature range, $(T_1 T_2)$ will not differ appreciably from T_0^2 , nor $\frac{(T_2 + T_1)}{2} T_1 T_2$ from T_0^3 , nor

$$\frac{(T_2^2 + T_1 T_2 + T_1^2)}{3} T_1 T_2$$

from T_0^4 . A comparison of temperatures where $T_1 = 0^\circ\text{C.}$ and $T_2 = 35^\circ\text{C.}$ shows that T_0 is 16.8°C. , while $(T_1 T_2)^{1/2} = 17.0^\circ\text{C.}$,

$$\left[\frac{(T_1 + T_2)}{2} T_1 T_2 \right]^{1/3} = 17.1^\circ\text{C.}$$

and

$$\left[\frac{(T_1^2 + T_1 T_2 + T_2^2)}{3} T_1 T_2 \right]^{1/4} = 17.3^\circ\text{C.}$$

the temperature range being not more than 0.5°C. , a fairly close approximation. The error introduced in ΔH for the temperature interval will be small, particularly if the constants c , d , and e are small.

On replacement of the above terms by T_0 as a close approximation, equation 8 becomes

$$\frac{RT_1T_2}{T_2 - T_1} \ln \frac{K_2}{K_1} = a + bT_0 + cT_0^2 + dT_0^3 + eT_0^4 \quad (9)$$

Combining with equation 6, equation 9 becomes identical with equation 5. In a similar manner it can be shown that equation 9 can be used for higher powers of T_0 .

We have shown therefore that, when ΔH is a linear, quadratic, cubic, or quartic function of temperature, equation 5 can be used as a very close approximation for the calculation of ΔH_0 at a temperature T_0 (as defined by equation 4) from the values for K at temperatures T_1 and T_2 . Such a calculation does not require any knowledge of the constant coeffi-

TABLE 1
Comparison of two methods for heat of ionization

ACID	T_1	T_2	$\frac{T_2 - T_1}{T_1}$	T_0	$K_1 \times 10^5$	$K_2 \times 10^5$	$\frac{\Delta H_0}{\text{(CALCULATED)}}$	$\frac{\Delta H}{\text{(CLASSICAL)}}$	$\frac{\Delta H_0 - \Delta H}{\text{calories}}$
	°C.	°C.	°C.	°C.			calories	calories	calories
Formic (6)	0	60	60	28.0	1.638	1.551	-165	-138	-27
Acetic (4)	0	60	60	28.0	1.657	1.542	-217	-215	-2
	0	25	25	12.1	1.657	1.754	368	316	52
Chloroacetic (19) . .	0	40	40	19.1	152.8	122.9	-926	-956	30
	0	25	25	12.1	152.8	137.8	-669	-681	12
Propionic (5)	0	60	60	28.0	1.274	1.160	-283	-283	0
n-Butyric (8)	0	35	35	16.8	1.563	1.439	-395	-338	-57
Sulfuric (second hydrogen) (3)	0	60	60	28.0	1480.	596.	-2742	-2509	-233
	0	25	25	12.1	1480.	1200.	-1357	-1116	-241
Glycine (K_A) (10)	10	45	35	26.8	394.	486.	1059	1102	43

cients, a , b , c , d , and e . The method is very useful in the determination of approximate values of ΔH at a given temperature when only one value of the heat of reaction is required and when only two values of K are known.

Table 1 shows that the heat of ionization (13) of the carboxylic acids obtained by the approximate method differs from that obtained by equation 6 or by similar procedures by a maximum of 57 cal. Since the variation of ΔH depends primarily upon the temperature interval selected and upon the value of the constant coefficients in the terms T^2 and T^3 , it would be expected that, if the coefficients were large enough to contribute several thousand calories, the difference in values obtained by the two methods, corresponding to a difference in T of 0.5°C ., would be large. Such is the case for the second hydrogen of sulfuric acid, for the higher order terms contribute appreciably to the value of ΔH_0 .

TABLE 2
Heats of ionization of some organic acids
 Temperature = 16.8°C., approximately

NO.	ACID	$K_1 \times 10^4$ (0°C.)	$K_2 \times 10^4$ (35°C.)	ΔH_0^* (16.8°C.)	ΔH^\dagger (CLASSICAL)
1	Benzoic (16).....	0.611	0.684	539	504
2	<i>m</i> -Nitrobenzoic (18).....	3.31	3.41	142	188
3	<i>p</i> -Nitrobenzoic (17).....	3.62	4.14	641	
4	3,5-Dinitrobenzoic (17).....	13.4	16.4	965	
5	<i>o</i> -Hydroxybenzoic (16).....	8.3	10.6	1169	
6	<i>m</i> -Hydroxybenzoic (16).....	0.725	0.789	404	333
7	<i>p</i> -Hydroxybenzoic (16).....	0.251	0.287	640	
8	2,4-Dihydroxybenzoic (17).....	3.95	5.25	1360	
9	2,5-Dihydroxybenzoic (17).....	10.4	12.9	1029	
10	Gallic (16).....	0.338	0.394	733	
11	<i>o</i> -Chlorobenzoic (17).....	13.7	11.9	-673	
12	<i>m</i> -Chlorobenzoic (11).....	1.41	1.54	421	
13	<i>p</i> -Chlorobenzoic (11).....	0.55	0.68	1014	
14	<i>m</i> -Bromobenzoic (11).....	1.33	1.55	731	
15	<i>o</i> -Toluic (16).....	1.59	1.25	-1150	-1060
16	<i>m</i> -Toluic (16).....	0.515	0.554	349	
17	<i>p</i> -Toluic (16).....	0.383	0.437	630	
18	Anisic (12).....	0.291	0.330	601	
19	Vanillic (12).....	0.300	0.355	804	
20	<i>m</i> -Acetoxybenzoic (11).....	1.19	1.32	495	
21	Acetylsalicylic (12).....	3.10	2.72	-625	
22	Cinnamic (16).....	0.322	0.363	573	
23	Hydrocinnamic (12).....	0.220	0.217	-66	
24	<i>o</i> -Coumaric (12).....	0.233	0.242	181	
25	Naphthionic (12).....	11.7	27.6	4101	
26	Camphoric (17).....	0.285	0.254	-550	
27	Benzilic (17).....	9.25	8.93	-168	
28	Mandelic (16).....	4.30	4.24	-67	
29	Levulinic (17).....	0.220	0.246	534	
30	Acetic (16).....	0.175	0.183	214	163
31	Phenylacetic (16).....	0.540	0.506	-311	
32	Cyanoacetic (17).....	38.7	34.8	-508	
33	Propionic (16).....	0.133	0.136	107	136

* The subscript zero does not refer to a standard state. ΔH_0 is calculated for $T_0 = 16.8^\circ\text{C}$.

† Reference 9.

TABLE 2—*Concluded*

NO.	ACID	$K_1 \times 10^4$ (0°C.)	$K_2 \times 10^4$ (35°C.)	ΔH_o^* (16.8°C.)	ΔH^\dagger (CLASSICAL)
34	α -Bromopropionic (17)	12.4	9.2	-1426	
35	β -Iodopropionic (17)	0.977	0.910	-450	
36	<i>n</i> -Butyric (16)	0.163	0.147	-494	
37	α -Bromobutyric (17)	14.98	11.5	-1263	
38	Isobutyric (16, 17)	0.155	0.142	-419	
39	Hydroxyisobutyric (17)	0.96	1.07	518	
40	Isovaleric (17)	0.167	0.141	-809	
41	Caprylic (17)	0.125	0.123	-77	
42	Crotonic (16)	0.199	0.211	280	
43	Phenylpropionic (8)	63.5	53.8	-792	

HEATS OF IONIZATION OF SOME ORGANIC ACIDS

The new method outlined above makes it possible to calculate, with a relatively small error, heats of ionization from dissociation constant data obtained at only two temperatures. The author observed that this method could be used to obtain some heats of ionization hitherto unknown, and that it could also be used to study the relationship of heat of ionization to ionization constant in various organic acids.

Table 2 presents in column 3 calculated heats of ionization which are new to the literature in most cases, as compared, in column 4, with values calculated by other methods. The values of K are the classical constants, rather than the thermodynamic values corrected to infinite dilution. The difference between the classical constant and the thermodynamic constant of weak organic acids is usually very small. *o*-Nitrobenzoic acid has not been included in the table, because it is so strong that Ostwald's dilution law does not hold even approximately and dilution has a marked effect upon K . In order to eliminate personal errors, only those values of K were used which were determined at different temperatures by the same worker. Table 2 shows that the values for ΔH obtained by the approximate method compare very favorably with those obtained by classical methods (9).

Figure 1 shows $\log K$ plotted against ΔH , the numbers on the graph corresponding with those of the acids listed in table 2. By use of the equation

$$-RT \ln K = \Delta H - T\Delta S \quad (10)$$

where R , T , K , and ΔH have the usual notation and ΔS represents the increase in entropy due to ionization, the variable most concerned in the change in structure of an organic acid, such as the introduction or substitution of groups or a change in resonance energy, may be studied.

Figure 1 shows that there is no simple relation between the ionization constant, K , and the heat of ionization, ΔH , of organic acids. The two constants seem to be in no way dependent upon each other. For example, the plotted points of benzoic acid, *m*-nitrobenzoic acid, and *p*-nitrobenzoic acid form an equilateral triangle, while those of benzoic acid and the three monohydroxybenzoic acids form a parallelogram.

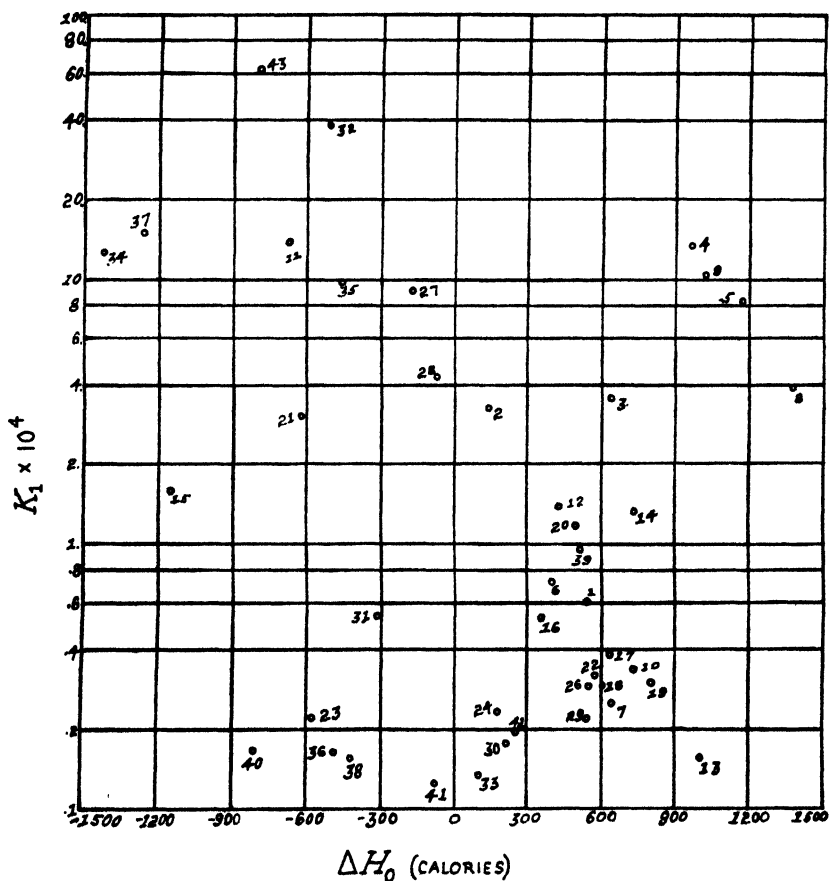


FIG. 1

Introduction of a hydroxyl group into the ortho position in benzoic acid and into *m*-hydroxybenzoic acid causes about the same change in ΔH and causes parallel changes in $\log K$ of the two compounds. Likewise, introduction of a hydroxyl group into the meta position in benzoic acid and into *o*-hydroxybenzoic acid (giving 2,5-dihydroxybenzoic acid) causes parallel changes in ΔH and in $\log K$, ΔH decreasing in both cases and $\log K$ increasing. Para-substitution of the hydroxyl group in benzoic acid

and in *o*-hydroxybenzoic acid (giving 2,4-dihydroxybenzoic acid) causes increases, though not parallel ones, in $\log K$ and decreases in ΔH . These changes are perhaps fortuitous, because gallic acid bears no such close relationship to either *m*-hydroxybenzoic acid or *p*-hydroxybenzoic acid.

The plot of the chlorobenzoic acids shows a linear relationship between ΔH and $\log K$. The stronger the acid, the lower the heat of ionization.

The saturated aliphatic acids have a narrow range of K (between 1×10^{-5} and 2×10^{-5}), but their heats of ionization range from -809 cal. to $+214$ cal.² Of the six listed in table 2, those of lower molecular weight have the higher heats of ionization except for caprylic acid, which lies between propionic and isobutyric acids. This fact might be interpreted to mean that the carbon chain of the caprylic acid molecule is folded. As might be expected, isobutyric acid with its more compact structure has a slightly higher heat of ionization than *n*-butyric acid.

Increase in the molecular weight of propionic acid by substituting a phenyl group on the omega carbon atom (hydroxycinnamic acid) causes the same sort of lowering in heat of ionization as noted above in saturated aliphatic acids. However, this relationship does not hold where polar groups are substituted on the aliphatic acids, since the heat of ionization of β -iodopropionic acid is higher than that of α -bromopropionic acid.

A comparison of isobutyric acid and hydroxyisobutyric acid shows that hydroxyl groups tend to increase the heat of ionization. A similar effect has been noted in the aromatic series when hydroxyl groups are substituted in the ortho and para positions.

It has been pointed out (1) that resonance energy plays an important part in the dissociation of ortho- and para-substituted benzoic acids. Table 2 shows that four different groups (including ortho-para orienting groups as well as so-called "electronegative" and "electropositive" groups)—methyl, hydroxyl, chloro, and nitro groups—raised the heat of ionization of benzoic acid when substituted in the para position. All except the hydroxyl group decrease the heat of ionization when substituted in the ortho position. It has been postulated (14) that numerous other factors influence the ionization of ortho-substituted derivatives.

The theory (1) leads one to expect that resonance energy is not concerned in the ionization of derivatives with one substituent in the meta position (15). The data in table 2 show that each of the four groups mentioned above caused a decrease in the heat of ionization when sub-

² These relationships cannot be expected to be very close, since dissociation constants at 0°C. were compared with ΔH values obtained at about 16.8°C. If both had been considered at the same temperature, a better interpretation could have been made. However, the data are not yet available.

stituted in the meta position of benzoic acid.³ It may therefore be said that in the absence of resonance effect the methyl, hydroxyl, chloro, and nitro groups contribute a decrease to the heat of ionization when substituted in the benzoic acid molecule. The increase in the heat of ionization when these groups are substituted in the para position must be due to increased resonance energy.

It may be said in general that, since specific heats of ionization are all of about the same order of magnitude, and since they vary negatively with an increase in temperature, the acids having the higher heats of ionization will reach maximum ionization at a higher temperature (7).

SUMMARY

1. A new approximation method for the calculation of the heats of ionization of organic acids has been presented.
2. Some new heats of ionization of organic acids have been calculated.
3. Resonance energy has been shown to increase the heats of ionization of certain substituted benzoic acids.
4. The relation between the heat of ionization and the ionization constant in certain organic acids has been presented.

REFERENCES

- (1) BRANCH, G. E. K., AND YABROFF, D. L.: J. Am. Chem. Soc. **56**, 2568 (1934).
- (2) DOUGLAS, T. B., AND CROCKFORD, H. D.: J. Am. Chem. Soc. **57**, 97 (1935).
- (3) HAMER, W. J.: J. Am. Chem. Soc. **56**, 860 (1934).
- (4) HARNED, H. S., AND EHLERS, R. W.: J. Am. Chem. Soc. **55**, 652 (1933).
- (5) HARNED, H. S., AND EHLERS, R. W.: J. Am. Chem. Soc. **55**, 2379 (1933).
- (6) HARNED, H. S., AND EMBREE, N. D.: J. Am. Chem. Soc. **56**, 1042 (1934).
- (7) HARNED, H. S., AND EMBREE, N. D.: J. Am. Chem. Soc. **56**, 1050 (1934).
- (8) HARNED, H. S., AND SUTHERLAND, R. O.: J. Am. Chem. Soc. **56**, 2039 (1934).
- (9) LANDOLT, H. H.: Landolt-Börnstein Physikalisch-Chemische Tabellen, Book II, pp. 1576-8. Julius Springer, Berlin (1923).
- (10) OWEN, B. B.: J. Am. Chem. Soc. **56**, 24 (1934).
- (11) SMITH, L. D., AND JONES, H. C.: Am. Chem. J. **50**, 1 (1913).
- (12) SPRINGER, A., AND JONES, H. C.: Am. Chem. J. **43**, 411 (1912).
- (13) WALDE, A. W.: J. Phys. Chem. **39**, 477 (1935).
- (14) WALDE, A. W.: J. Phys. Chem. **39**, 885 (1935).
- (15) WHELAND, G. W., AND PAULING, L.: J. Am. Chem. Soc. **57**, 2086 (1935).
- (16) WHITE, G. F., AND JONES, H. C.: Am. Chem. J. **44**, 159 (1910).
- (17) WIGHTMAN, E. D., AND JONES, H. C.: Am. Chem. J. **43**, 56 (1911).
- (18) WIGHTMAN, E. D., AND JONES, H. C.: Am. Chem. J. **43**, 320 (1912).
- (19) WRIGHT, D. D.: J. Am. Chem. Soc. **56**, 314 (1934).

³ *m*-Bromobenzoic acid and *m*-dinitrobenzoic acid have higher values for ΔH than does benzoic acid, perhaps owing to the effect of increased molecular weight. Obviously more exhaustive study is necessary before drawing rigid conclusions.

FIG. 1. Relation of ionization constants of some organic acids to heats of ionization

THE VISCOSITY OF DILUTE SOLUTIONS OF LONG-CHAIN MOLECULES. II¹

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In the first paper of this series (4) there were given, without detailed derivation, equations relating the specific viscosity, η_{sp} , of a dilute solution to the concentration and the coördinates and sizes of the atoms in the solute molecules. The derivations will now be supplied.

DERIVATION OF THE GENERAL EQUATION

The procedure is an extension of that used by Kuhn (5) in deriving an equation for the viscosity of a rod-like molecule. Considering any rigid solute molecule, let the coördinates of the n component atoms, measured relative to rectangular axes passing through the center of moments, be designated as x_i, y_i, z_i . The surrounding liquid is assumed to be moving in the z direction with a velocity (relative to that at the molecule center) qx , which is proportional to x (figure 1).

The velocity gradient causes the molecule (if not spherical) to rotate around the Y -axis. In spite of such rotation, however, each atom is, in general, not moving with the same velocity as the liquid immediately surrounding it. After calculating this relative velocity, one assumes Stokes' law to obtain the work done by the atom on the liquid, and, after suitable summation and averaging, the increase in viscosity resulting from the velocity gradient.

Defining R_i, r_i , and θ_i as indicated in figure 1,

$$x_i = r_i \cos \theta_i \quad (1)$$

$$z_i = r_i \sin \theta_i \quad (2)$$

$$\dot{x}_i = -z_i \dot{\theta}_i \quad (3)$$

and

$$\dot{z}_i = x_i \dot{\theta}_i \quad (4)$$

The velocity of atom i relative to the immediately surrounding liquid is

$$u_i = \sqrt{u_{x,i}^2 + u_{z,i}^2} \quad (5)$$

¹ Communication No. 690 from the Kodak Research Laboratories.

where

$$u_{z,i} = -z_i \dot{\theta}_i \quad (6)$$

and

$$u_{x,i} = x_i (\dot{\theta} - q) \quad (7)$$

The force acting on this atom, according to Stokes' law, has the direction $-u_i$ and the magnitude

$$|K_i| = 6 \pi \eta a_i u_i \quad (8)$$

Its components in the X and Z directions are:

$$K_{x,i} = 6 \pi \eta a_i z_i \dot{\theta}_i \quad (9)$$

and

$$K_{z,i} = -6 \pi \eta a_i x_i (\dot{\theta}_i - q) \quad (10)$$

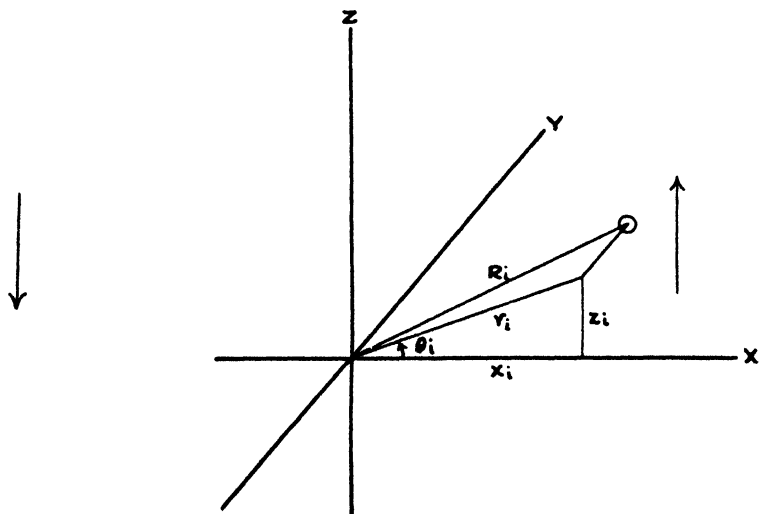


FIG. 1. Illustrating the orientation of reference axes, etc.

η is the viscosity of the solution and a_i is the "effective radius" of atom i . This effective radius is smaller than the true radius if the atoms in the molecule are not well separated from each other. (Concerning the estimation of a_i , see the discussion at the end of this paper.)

The moment acting on atom i , tending to rotate the molecule, is

$$\dot{M}_i = K_{x,i} z_i - K_{z,i} x_i = 6 \pi \eta a_i (r_i^2 \dot{\theta}_i - x_i^2 q) \quad (11)$$

For no acceleration or deceleration of the rotation,

$$\sum M_i = 0 \quad (12)$$

the summation (here and elsewhere in this paper unless otherwise specified) being over all the n atoms of the molecule. Hence

$$\sum a_i(r_i^2 \theta_i - x_i^2 q) = 0 \quad (13)$$

For a rigid molecule θ_i is the same for all the atoms, hence the subscript can be dropped. Solving for θ ,

$$\theta = \frac{q \sum a_i x_i^2}{\sum a_i r_i^2} = \frac{q \sum a_i r_i^2 \cos^2 \theta_i}{\sum a_i r_i^2} \quad (14)$$

The energy loss in unit time, due to atom i , is

$$\epsilon_i = |K_i| |u_i| = 6\pi\eta q^2 a_i \frac{z_i^2 (\sum a_i x_i^2)^2 + x_i^2 (\sum a_i z_i^2)^2}{(\sum a_i r_i^2)^2} \quad (15)$$

by substituting into equations 5, 6, 7, and 8. The energy loss per unit of time for the whole molecule is

$$\epsilon = \sum \epsilon_i = 6\pi\eta q^2 F'_{zz} \quad (16)$$

where

$$F'_{zz} = \frac{\sum a_i x_i^2 \cdot \sum a_i z_i^2}{\sum a_i r_i^2} = \frac{\sum a_i r_i^2 \cos^2 \theta_i \cdot \sum a_i r_i^2 \sin^2 \theta_i}{\sum a_i r_i^2} \quad (17)$$

If all the atoms in the molecule have the same radius, a ,

$$\epsilon = 6\pi\eta q^2 a F_{zz} \quad (18)$$

$$F_{zz} = \frac{\sum x_i^2 \cdot \sum z_i^2}{\sum r_i^2} = \frac{\sum r_i^2 \cos^2 \theta_i \cdot \sum r_i^2 \sin^2 \theta_i}{\sum r_i^2} \quad (19)$$

The energy loss due to all the solute molecules, per cubic centimeter of solution, is

$$E_2 = c' N \bar{\epsilon} = 6\pi N c' q^2 \eta \overline{F'_{zz}} \quad (20)$$

N is Avogadro's number, c' is the concentration in moles per cubic centimeter, and $\overline{F'_{zz}}$ is the average of F'_{zz} over all the solute molecules.

The number of solvent molecules per cubic centimeter of solution (assuming that the average volume of a solvent molecule is the same in the solution as in the pure solvent and that the density of the solvent is the same as that of the solution) is $\left(1 - \frac{v}{V}\right)$ times the number of solvent molecules per cubic centimeter of pure solvent. V is the volume of the solution and v is the volume occupied by solute molecules. The energy transformed to heat per cubic centimeter of pure solvent is $q^2 \eta_0$, where η_0 is the viscosity of the pure solvent. Therefore the energy loss due to the *solvent* molecules in 1 cc. of solution is

$$E_1 = q^2 \eta_0 \left(1 - \frac{v}{V}\right) \quad (21)$$

If the solute molecules are very similar in size and shape to the solvent molecules, the viscosity of the solution is the same as that of the pure solvent. The energy loss due to the *solute* molecules in 1 cc. of solution is, in this case,

$$E_s = q^2 \eta_0 \left(\frac{v}{V} \right) \quad (22)$$

If, however, the solute molecules are large and spherical, their contribution is

$$E_s = 3.5q^2 \eta_0 \left(\frac{v}{V} \right) \quad (23)$$

to give agreement with Einstein's viscosity law, which requires

$$E_1 + E_s = q^2 \eta_0 \left(1 + \frac{5}{2} \frac{v}{V} \right) \quad (24)$$

In general, one may write

$$E_s = (1 + k_E)q^2 \eta_0 \left(\frac{v}{V} \right) \quad (25)$$

where k_E is a constant, depending on the relative sizes and shapes of solvent and solute molecules.

For chain molecules in which the size of the units linked together (e.g., the $\text{—CH}_2\text{—}$ units in a normal paraffin) is of the same order of magnitude as the size of the solvent molecules, k_E would be expected to have a value close to zero, especially if the chain is somewhat flexible. Its sign might be either positive or negative,—the latter for relatively large solvent molecules.

The viscosity of the solution is given by the equation

$$\eta = \frac{E_1 + E_2 + E_s}{q^2} = \eta_0 \left(1 + \frac{k_E v}{V} \right) + \eta(6\pi N c' \overline{F'_{zs}}) \quad (26)$$

Hence,

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1 = \frac{k_E \frac{v}{V} + 6\pi N c' \overline{F'_{zs}}}{1 - 6\pi N c' \overline{F'_{zs}}} \quad (27)$$

The next problem is to calculate $\overline{F'_{zs}}$, making use of equation 17 for F'_{zs} . We put

$$\theta_i = \theta'_i + \theta_0 \quad (28)$$

the θ'_i values being constants, measured relative to a set of axes (X' , Z') rotating with the molecule. These axes are so chosen as to make

$$\sum a_i r_i^2 \cos \theta'_i \sin \theta'_i = 0 \quad (29)$$

Therefore,

$$\cos^2 \theta_i = \cos^2 \theta'_i \cos^2 \theta_0 + \sin^2 \theta'_i \sin^2 \theta_0 \quad (30)$$

$$\sin^2 \theta_i = \sin^2 \theta'_i \cos^2 \theta_0 + \cos^2 \theta'_i \sin^2 \theta_0 \quad (31)$$

Substituting in equation 17,

$$\overline{F'_{zz}} = \left[\frac{CS}{\Sigma a_i r_i^2} (\cos^4 \theta_0 + \sin^4 \theta_0) + \frac{(C^2 + S^2)}{\Sigma a_i r_i^2} \cos^2 \theta_0 \sin^2 \theta_0 \right] \quad (32)$$

where

$$C = \Sigma a_i r_i^2 \cos^2 \theta'_i \quad (33)$$

and

$$S = \Sigma a_i r_i^2 \sin^2 \theta'_i \quad (34)$$

Let ρ be the average fraction of the total number of molecules having a value of θ_0 between θ_0 and $\theta_0 + d\theta_0$. Alternatively, ρ can be defined as the fraction of the time, on the average, that θ_0 for any given molecule is between θ_0 and $\theta_0 + d\theta_0$. The following relation then holds:

$$\overline{F'_{zz}} = \left\{ \int_0^{2\pi} \rho \left[\frac{CS}{\Sigma a_i r_i^2} (\cos^4 \theta_0 + \sin^4 \theta_0) + \frac{C^2 - S^2}{\Sigma a_i r_i^2} \cos^2 \theta_0 \sin^2 \theta_0 \right] d\theta_0 \right\}_{\text{ave.}} \quad (35)$$

The integration takes care of the averaging over all values of θ_0 but not over all orientations of the molecules relative to the $XZX'Z'$ plane.

The function ρ depends on the relative magnitude of the velocity gradient q , which tends to favor orientation of elongated molecules with their long axes parallel to the Z -axis, and the Brownian motion, which tends to make all orientations equally probable.

If the Brownian motion is of negligible importance, as compared with q , ρ is inversely proportional to θ , as given by equation 14. The proportionality constant is deduced from the relation

$$\int_0^{2\pi} \rho d\theta_0 = 1 \quad (36)$$

making use of equation 30 and the integral (3)

$$\int_0^{2\pi} \frac{d\theta_0}{C \cos^2 \theta_0 + S \sin^2 \theta_0} = \frac{2\pi}{\sqrt{CS}} \quad (37)$$

one obtains

$$\rho = \frac{\sqrt{CS}}{2\pi(C \cos^2 \theta_0 + S \sin^2 \theta_0)} \quad (38)$$

For a negligible velocity gradient q or very strong Brownian motion, all values of θ_0 are equally probable and

$$\rho = \frac{1}{2\pi} \quad (39)$$

To obtain a second approximation, for the case of strong Brownian motion, one may follow Kuhn (reference 5, pages 11, 12) in calculating a "rotational diffusion constant," obtaining

$$D = \frac{kT}{6\pi\eta \sum a_i r_i^2} \quad (40)$$

in which k is Boltzmann's constant. Then, considering the superposition of the rotation due to the velocity gradient and the diffusion resulting from the Brownian motion, one deduces

$$\rho\theta - \frac{d\rho}{d\theta} \cdot D = \text{constant} \quad (41)$$

Substituting the value of θ as given by equations 14 and 30 leads to the equation

$$\frac{d\rho}{d\theta} + \alpha\rho \sin^2 \theta_0 = \text{constant} \quad (42)$$

where

$$\alpha = \frac{6\pi\eta q(C - S)}{kT} \quad (43)$$

Following Boeder (1), one then finds for ρ :

$$\rho = \frac{1}{2\pi} \left[1 + \alpha \frac{\sin^2 \theta_0}{4} + \alpha^2 \left(\frac{\cos 2\theta_0}{16} - \frac{\cos 4\theta_0}{64} \right) + \text{terms in higher powers of } \alpha \right] \quad (44)$$

$$= \frac{1}{2\pi} \left[1 + \alpha \frac{\sin \theta_0 \cos \theta_0}{2} + \alpha^2 \left(\frac{3}{64} - \frac{\sin^4 \theta_0}{8} \right) + \text{terms in higher powers of } \alpha \right] \quad (45)$$

Substituting equation 38 into equation 35 and integrating gives

$$\overline{F'_{zz}} = \frac{(\sqrt{CS})_{\text{ave.}}}{2} \quad (46)$$

for the case of negligible Brownian motion.

Substituting equation 45 into equation 35 leads to

$$\begin{aligned} \overline{F'_{zz}} = & \left[\frac{(\sum a_i r_i^2)_{\text{ave.}}}{8} + \frac{1}{2} \left(\frac{CS}{\sum a_i r_i^2} \right)_{\text{ave.}} \right] \\ & + \alpha^2 \left[\frac{(\sum a_i r_i^2)_{\text{ave.}}}{1024} - \frac{1}{256} \left(\frac{CS}{\sum a_i r_i^2} \right)_{\text{ave.}} \right] + \text{terms in higher powers of } \alpha \quad (47) \end{aligned}$$

for strong Brownian motion. In the limit, when α is zero,

$$\overline{F'_{zs}} = \frac{(\sum a_i r_i^2)_{\text{ave.}}}{8} + \frac{1}{2} \left(\frac{CS}{\sum a_i r_i^2} \right)_{\text{ave.}} \quad (48)$$

If one does not choose the X' - and Z' -axes so as to make equation 29 true, one obtains, in place of equation 48,

$$\overline{F'_{zs}} = \frac{(\sum a_i r_i^2)_{\text{ave.}}}{8} + \frac{1}{2} \left[\frac{CS - (\sum a_i r_i^2 \cos \theta'_i \sin \theta'_i)^2}{\sum a_i r_i^2} \right]_{\text{ave.}} \quad (49)$$

Equations 27, 46, 47, and 48 will now be applied to certain special cases.

ROD-LIKE CHAIN MOLECULES

Consider a hypothetical rigid, rod-like chain molecule, such as represented in figure 2. Let X' - and Z' -axes be so chosen that the molecular axis is

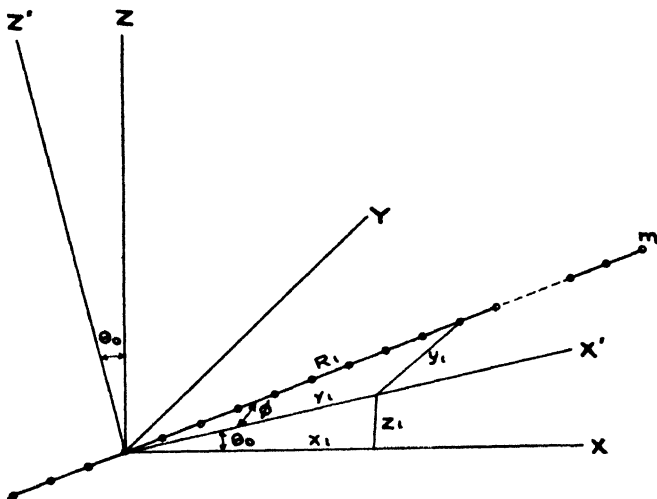


FIG. 2. Illustrating the orientation of axes, etc., for a rigid rod-like molecule

in the $X'Y$ plane. All the θ'_i values are then either 0 or π . Equation 29, therefore, holds. Also

$$C = \sum a_i r_i^2 \cos^2 \theta'_i = \sum a_i r_i^2 \quad (50)$$

and

$$S = \sum a_i r_i^2 \sin^2 \theta'_i = 0 \quad (51)$$

For no Brownian motion, from equation 46,

$$\overline{F'_{zs}} = 0 \quad (52)$$

and, from equation 27,

$$\eta_{sp} = k_B \frac{v}{V} \quad (53)$$

All the solute molecules would, for this limiting case, align themselves with their axes parallel to the Z -axis, their rotational velocity then being zero. (This result would not have been obtained if the difference in velocity of the solvent on opposite sides of *each atom* had been allowed for. One would still find, however, that $F'_{zz} \approx 0$.) (54)

Following Staudinger (7) in defining c as the concentration in submoles ("Grundmole") per liter (identical in the present instance with gram-atoms per liter),

$$c = 1000nc' \quad (55)$$

and

$$\frac{v}{V} = \frac{cM_0}{1000\rho} \quad (56)$$

M_0 is the "molecular weight" of a submole (in this case the atomic weight) and ρ is the density of the pure liquid solute in grams per cubic centimeter. Substituting in equation 53,

$$\frac{\eta_{sp}}{c} \approx \frac{k_B M_0}{1000\rho} \approx 0 \quad (57)$$

For strong Brownian motion or zero velocity gradient, i.e., for small values of α (equation 43), substitution in equation 47 gives

$$\overline{F'_{zz}} = (\sum a_i r_i^2)_{\text{ave.}} \left(\frac{1}{8} + \frac{\alpha^2}{1024} + \text{terms in higher powers of } \alpha \right) \quad (58)$$

$$= (a \overline{\cos^2 \phi} \sum R_i^2) \left(\frac{1}{8} + \frac{\alpha^2}{1024} + \dots \right) \quad (59)$$

where ϕ is the angle the molecule axis makes with the $XZX'Z'$ plane. If all orientations are equally probable

$$\overline{\cos^2 \phi} = \frac{2}{3} \quad (60)$$

Assuming for simplicity that the chain contains an odd number ($n = 2m + 1$) of atoms,

$$\sum R_i^2 = 2 \sum_1^m l^2 i^2 = \frac{l^2 m(m+1)(2m+1)}{3} = \frac{l^2}{12} (n^2 - n) \quad (61)$$

Hence,

$$\overline{F'_{zz}} = \frac{l^2 a (n^3 - n)}{18} \left(\frac{1}{8} + \frac{\alpha^2}{1024} + \dots \right) \quad (62)$$

and, from equations 27, 55, and 56,

$$\frac{\eta_{sp}}{c} = \frac{\frac{k_B M_0}{1000 \rho} + \frac{\pi N l^2 a (n^2 - 1)}{3000} \left(\frac{1}{8} + \frac{\alpha^2}{1024} + \dots \right)}{1 - \frac{\pi N l^2 a (n^2 - 1)}{3000} \left(\frac{1}{8} + \frac{\alpha^2}{1024} + \dots \right) c} \quad (63)$$

Approximately,

$$\frac{\eta_{sp}}{c} = \frac{\pi N l^2 a n^2}{24000} \quad (64)$$

If, following Kuhn (5), one takes the volume of the molecule as that of a cylinder of length nl and diameter $2a$, equation 64 can be transformed to

$$\eta_{sp} = \frac{n^2 l}{24a} \cdot \frac{v}{\bar{V}} \quad (65)$$

For the special case treated by Kuhn, in which $l = 4a$, this becomes

$$\eta_{sp} = \frac{1}{24} \left(\frac{nl}{2a} \right)^2 \frac{v}{\bar{V}} \quad (66)$$

which is equivalent to his equation 38 except for a factor, $2/3$, which has been introduced here (see equation 60) to allow for molecular orientations other than in the XZ plane, and except for his inclusion of the Einstein term, $\frac{5}{2} \frac{v}{\bar{V}}$.

If one takes the volume of the molecule as the sum of the volumes of n spheres of radius a , equation 64 leads to

$$\eta_{sp} = \frac{1}{8} \left(\frac{nl}{2a} \right)^2 \frac{v}{\bar{V}} \quad (67)$$

RIGID, RANDOMLY KINKED CHAIN MOLECULES

Consider next a rigid chain molecule which is centrosymmetric and which has constant equal bond angles and bond distances, but is otherwise randomly kinked (figure 3).

The average value of the square of the distance from the atom at the molecular center (the origin) to any other atom, i , according to a relationship derived by Eyring (2), is

$$\overline{R_i^2} = B_i l^2 i \quad (68)$$

where

$$B_i = 1 + 2 \binom{i-1}{i} \xi + 2 \binom{i-2}{i} \xi^2 + 2 \binom{i-3}{i} \xi^3 + \dots + 2\xi^{i-1} \quad (69)$$

and

$$\xi = \cos \alpha \quad (70)$$

The included angle between adjacent bonds is $(\pi - \alpha)$.

The expression for B_i can also be put in the form

$$B_i = \frac{1 + \xi}{1 - \xi} - \frac{2\xi}{(1 - \xi)^2} \cdot \frac{1}{i} + \frac{2\xi^{i+1}}{(1 - \xi)^2} \cdot \frac{1}{i} \quad (71)$$

$$\approx \frac{1 + \xi}{1 - \xi} \quad \text{for large } i \quad (72)$$

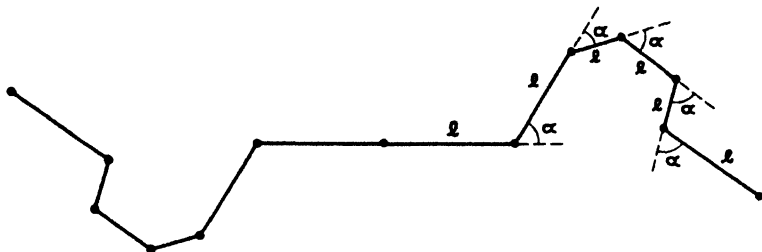


FIG. 3. Representing a randomly kinked, centrosymmetric molecule

For random orientation with respect to the angles ϕ_i , with all a_i values equal,

$$(\sum a_i r_i^2)_{\text{ave.}} = a \overline{\cos^2 \phi_i} \sum \overline{R_i^2} \quad (73)$$

$$= \frac{2}{3} a \sum \overline{R_i^2} \quad (74)$$

$$= \frac{4}{3} l^2 a \sum_1^m B_i i \quad (75)$$

the summation being over half of the chain only. Performing the summation, one obtains

$$(\sum a_i r_i^2)_{\text{ave.}} = \frac{2l^2 a B'}{3} m^2 = \frac{l^2 a B' (n^2 - 2n + 1)}{6} \quad (76)$$

with

$$B' = \left(\frac{1 + \xi}{1 - \xi} \right) \left(1 + \frac{1}{m} \right) - \frac{4\xi}{m(1 - \xi)^2} + \frac{4\xi^2(1 - \xi^m)}{m^2(1 - \xi)^3} \quad (77)$$

To calculate the other quantities needed for substitution into equations 46 and 48, one chooses the X' - and Z' -axes so that the projections on the

$XX'Z'$ plane of the end atoms of the chain lie on the X' -axis. Although this choice does not make $\sum a_i r_i^2 \cos \theta'_i \sin \theta'_i$ equal to zero, as required by equation 29, it can be shown that

$$CS \approx 6m(\sum a_i r_i^2 \cos \theta'_i \sin \theta'_i)^2 \quad (78)$$

The error introduced in using equation 48 rather than equation 49 is thus negligible. One would likewise expect the inexactness of equation 46 resulting from this choice of axes to be negligible.

Kuhn (6) has calculated statistically the probability that the middle atom in a randomly kinked chain of $(m + 1)$ atoms is a distance S_i away

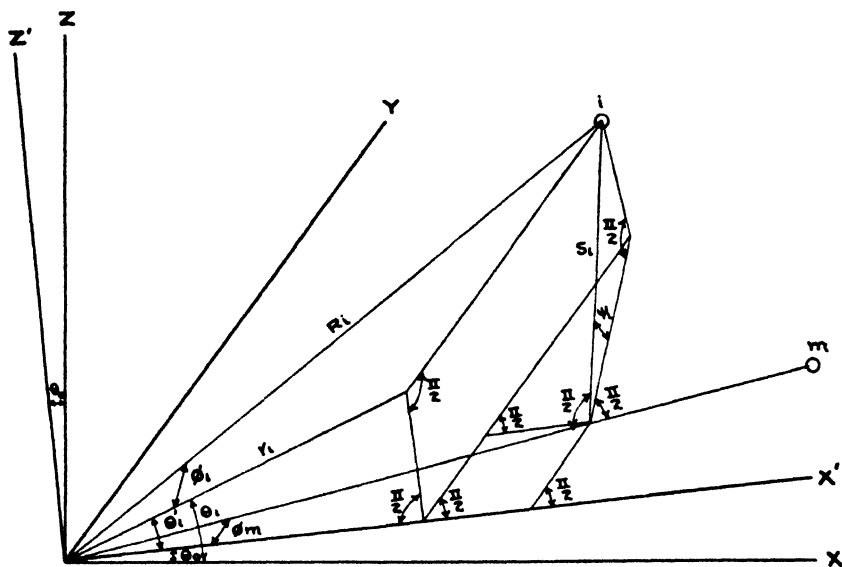


FIG. 4. Illustrating the notation used

from the straight line joining the end atoms. Extending his treatment, one can show that the probability that the i th atom in such a chain is a distance S_i from the line joining the ends is given by the equation

$$W_{S_i} = \frac{3mS_i}{B_i l^2 i(m-i)} e^{-\frac{3mS_i^2}{2B_i l^2 i(m-i)}} \quad (79)$$

Here B_i is the function given by equation 69. Averaging in the usual manner one obtains

$$\overline{S_i^2} = \frac{2B_i l^2}{3} \left(i - \frac{i^2}{m} \right) \quad (80)$$

If one designates by ϕ_m the angle the molecular axis (through the center and end atoms) makes with the X' -axis and, by ψ_i , the angle which the

perpendicular from the i th atom to the molecular axis makes with the $X'Y$ plane (see figure 4),

$$\overline{\gamma_i^2 \cos^2 \theta_i'} = \overline{[(R_i^2 - S_i^2)^{1/2} \cos \phi_m - S_i \cos \psi_i \sin \phi_m]^2} \quad (81)$$

$$= \overline{(R_i^2 - S_i^2) \cos^2 \phi_m} + \overline{S_i^2 \cos^2 \psi_i \sin^2 \phi_m} \\ - \overline{2S_i(R_i^2 - S_i^2)^{1/2} \cos \psi_i \sin \phi_m \cos \phi_m} \quad (82)$$

$$= \overline{(R_i^2 - S_i^2) \cos^2 \phi_m} + \overline{S_i^2 \cos^2 \psi_i \sin^2 \phi_m} \\ - \overline{2S_i(R_i^2 - S_i^2)^{1/2} \cos \psi_i \sin \phi_m \cos \phi_m} \quad (83)$$

All values of ψ_i are equally probable, hence

$$\overline{\cos \psi_i} = 0 \quad (84)$$

$$\overline{\cos^2 \psi_i} = \frac{1}{2} \quad (85)$$

The probability of a given value of ϕ_m is proportional to $\cos \phi_m$, assuming random orientation of the molecules with regard to orientation relative to the XZ plane. Taking this into account,

$$\overline{\cos^2 \phi_m} = \frac{2}{3} \quad (86)$$

and

$$\overline{\sin^2 \phi_m} = \frac{1}{3} \quad (87)$$

Substituting in equation 83 gives

$$\overline{r_i^2 \cos^2 \theta_i'} = \frac{2\overline{R_i^2}}{3} - \frac{\overline{S_i^2}}{2} \quad (88)$$

$$= \frac{B_i l^2}{3} \left(i + \frac{i^2}{m} \right) \quad (89)$$

Similarly,

$$\overline{r_i^2 \sin^2 \theta_i'} = \frac{\overline{S_i^2}}{2} \quad (90)$$

$$= \frac{B_i l^2}{3} \left(i - \frac{i^2}{m} \right) \quad (91)$$

Summing, one obtains

$$\overline{C} = \frac{2l^2 a}{3} \left(\sum_1^m B_i i + \frac{1}{m} \sum_1^m B_i i^2 \right) \quad (92)$$

$$= \frac{2l^2 a m^2}{3} \left(\frac{B'}{2} + \frac{B''}{3} \right) \quad (93)$$

and

$$\bar{S} = \frac{2l^2 a}{3} \left(\sum_1^m B_i i - \frac{1}{m} \sum_1^m B_i i^2 \right) \quad (94)$$

$$= \frac{2l^2 a m^2}{3} \left(\frac{B'}{2} - \frac{B''}{3} \right) \quad (95)$$

where B' is given by equation 77 and

$$B'' = \left(\frac{1+\xi}{1-\xi} \right) \left(1 + \frac{3}{2m} + \frac{1}{2m^2} \right) - \frac{3\xi}{(1-\xi)^2} \left(\frac{1}{m} + \frac{1}{m^2} \right) - \frac{6\xi^2 \xi^m}{m^2(1-\xi)^3} + \frac{6\xi^2(1-\xi^m)}{m^3(1-\xi)^4} \quad (96)$$

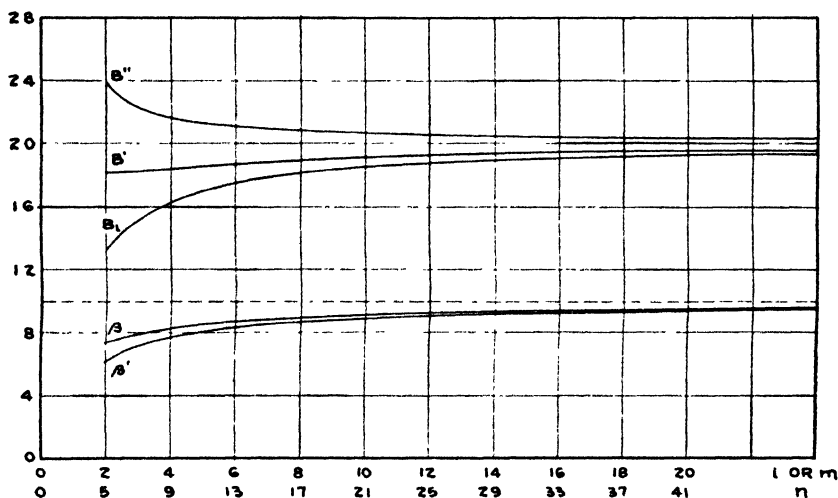


FIG. 5. Variation of B , with i and of B' , B'' , β , and β' with m and with n , all for tetrahedral bond angles.

Making the approximations that

$$(\sqrt{CS})_{\text{ave.}} = \sqrt{C \cdot S} \quad (97)$$

and

$$\left(\frac{CS}{\sum a_i r_i^2} \right)_{\text{ave.}} = \frac{C \cdot S}{(\sum a_i r_i^2)_{\text{ave.}}} \quad (98)$$

one now substitutes equations 76, 93, and 95 into equations 46 and 47.

For negligible Brownian motion,

$$\bar{F}_{ss} = \frac{l^2 a m^2}{3} \left(\frac{B'^2}{4} - \frac{B''^2}{9} \right)^{1/2} \quad (99)$$

For strong Brownian motion or small velocity gradient,

$$\overline{F'_{zz}} = l^2 am^2 \left(\frac{B'}{6} - \frac{B''^2}{27B'} + \frac{\alpha^2 B''}{3456B'} + \dots \right) \quad (100)$$

Both B' and B'' approach the value

$$B_{\infty} = \left(\frac{1 + \xi}{1 - \xi} \right) \quad (101)$$

as m becomes large (see figure 5). Introducing the function

$$\beta' = \left(\frac{9}{5} \frac{B'^2}{B_{\infty}^2} - \frac{4}{5} \frac{B''^2}{B_{\infty}^2} \right)^{1/2} \quad (102)$$

Equation 99 can be written

$$\overline{F'_{zz}} = \frac{\sqrt{5}}{18} l^2 am^2 B_{\infty} \beta' \quad (103)$$

$$= 0.0311 l^2 a (n^2 - 2n + 1) B_{\infty} \beta' \quad (104)$$

$$\approx 0.0311 l^2 a n^2 B_{\infty} \text{ for large } n \quad (105)$$

Likewise, putting

$$\beta = \frac{9}{7} \frac{B'}{B_{\infty}} - \frac{2}{7} \frac{B''^2}{B' B_{\infty}} \quad (106)$$

and making the approximation in the small α^2 term that

$$B' = B'' = \beta B_{\infty} \quad (107)$$

equation 100 becomes

$$\overline{F'_{zz}} = \frac{7}{54} l^2 am^2 B_{\infty} \beta \left(1 + \frac{\alpha^2}{448} \right) \quad (108)$$

$$= 0.0324 l^2 a (n^2 - 2n + 1) B_{\infty} \beta \left(1 + \frac{\alpha^2}{448} \right) \quad (109)$$

For large n and small α this reduces to

$$\overline{F'_{zz}} = 0.0324 l^2 a n^2 B_{\infty} \quad (110)$$

Both β and β' approach unity as m increases, as shown in figure 5.

The axes of rotation for randomly kinked chain molecules which are not centrosymmetrical do not, in general, pass through the midpoints of the chain. $\overline{F'_{zz}}$ is, therefore, smaller than for otherwise similar molecules which do have centers of symmetry.

It is desired to find the average $\overline{F'_{zz}}$ for non-symmetrical kinked molecules, the coördinates of the atoms in each molecule being relative to a

Y-axis so situated as to make the $\overline{F'_{zz}}$ (and hence $\bar{\epsilon}$) for that molecule a minimum. There seems to be no easy direct way of calculating this average. A reasonable approximation, however, can be obtained in the following manner:

Let a quantity G' be defined by the equation

$$G' = \sum a_i M_i r_i \quad (111)$$

in which a_i is the radius of the i th atom, M , its mass, and r , the distance from the origin to its projection on the XZ plane. For a long, straight, rod-like molecule, composed of $n = 2m + 1$ like, equally spaced atoms, all in the XZ plane,

$$G' = 2laM_0 \sum_{i=1}^m i \approx \frac{laM_0 n^2}{4} \quad (112)$$

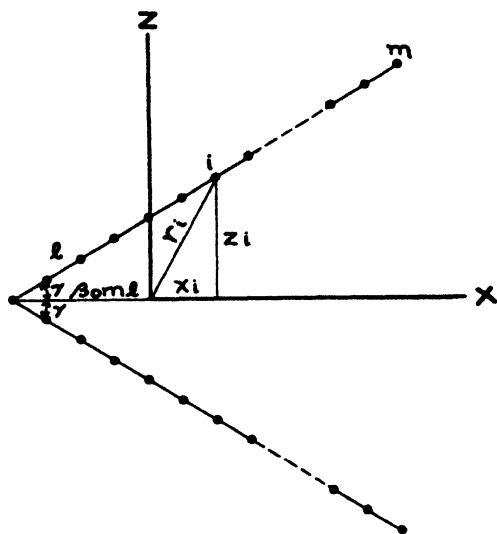


FIG. 6. Illustrating notation for a bent rod-like molecule

Comparing this with equations 105 and 110, one notes that G' for this long rod-like molecule and $\overline{F'_{zz}}$ for a large centrosymmetric kinked molecule become identical if we put

$$M_0 = 0.1244B_\infty l \quad \text{or} \quad 0.1296B_\infty l \quad (113)$$

The angle between the straight lines joining the middle of a randomly kinked chain molecule with its two ends may have any value from 0 to π . For a sufficiently long chain, all relative orientations in space of these two lines are equally probable, and the probability of any given included angle is proportional to the sine of that angle. It seems reasonable to assume that the desired average $\overline{F'_{zz}}$ for centrosymmetrical kinked mole-

cules is related to $\overline{F'_{xx}}$ for *unsymmetrical* kinked molecules in the same way as G' for a *straight* rod-like molecule is related to the G' for a rod-like molecule of the same length *bent in the middle* (figure 6), taking the probability of each bending angle as proportional to the sine of that angle and measuring the r values (for each bending angle) relative to such an origin as leads to the minimum value of G' .

This origin is obviously on the line bisecting the two legs of the molecule. One chooses this line as the X -axis and calls the distance from the joint to the origin $\beta_0 ml$. Then, neglecting the contribution of the atom at the bend,

$$G' = 2aM_0 \sum_1^m r_i \quad (114)$$

$$= 2aM_0 \sum_1^m (x_i^2 + z_i^2)^{1/2} \quad (115)$$

$$= 2aM_0 \sum_1^m (i^2 - 2\beta_0 m_i \cos \gamma + \beta_0^2 m^2)^{1/2} \quad (116)$$

Putting

$$i = \lambda m \quad (117)$$

one gets

$$G' = 2laM_0 m \sum_{\lambda=\frac{1}{m}}^1 (\lambda^2 - 2\beta_0 \lambda \cos \gamma + \beta_0^2)^{1/2} \quad (118)$$

For large m ,

$$G' = 2laM_0 m^2 \int_0^1 (\lambda^2 - 2\beta_0 \lambda \cos \gamma + \beta_0^2)^{1/2} d\lambda \quad (119)$$

$$= laM_0 m^2 \Psi \quad (120)$$

where

$$\begin{aligned} \Psi = & (1 - \beta_0 \cos \gamma)(1 - 2\beta_0 \cos \gamma + \beta_0^2)^{1/2} + \beta_0^2 \cos \gamma \\ & + \beta_0^2 \sin^2 \gamma \cdot \ln \left[\frac{(1 - 2\beta_0 \cos \gamma + \beta_0^2)^{1/2} - (1 - \beta_0 \cos \gamma)}{\beta_0(1 - \cos \gamma)} \right] \end{aligned} \quad (121)$$

For any given value of γ , values of Ψ as a function of β can be computed and the minimum value, $\Psi_{\min.}$, obtained. This varies from 1/2 for $\gamma = 0$ to 1 for $\gamma = \pi/2$. The average value of $\Psi_{\min.}$, making allowance for the $\sin 2\gamma$ probability factor, was determined graphically to be 0.81, or (within the accuracy of the calculation) 4/5. Without the $\sin 2\gamma$ factor, the average was 0.80.

Introducing the factor 4/5 into equation 104 gives, for negligible Brownian motion or large velocity gradient,

$$\overline{F'_{xx}} = \frac{1}{18\sqrt{5}} l^2 a B_{\infty} \beta' (n^2 - 2n + 1) \quad (122)$$

Substituting this and equations 55 and 56 into equation 27,

$$\frac{\eta_{sp}}{c} = \frac{\frac{k_B M_0}{1000\rho} + \frac{\pi N l^2 a B_\infty \beta' \left(n - 2 + \frac{1}{n}\right)}{3\sqrt{5} \cdot 1000}}{1 - \frac{\pi N}{3\sqrt{5} \cdot 1000} l^2 a B_\infty \beta' \left(n - 2 + \frac{1}{n}\right) c} \quad (123)$$

For large n , small k_B , and small c , giving N the value 6.024×10^{23} ,

$$\frac{\eta_{sp}}{c} \approx 2.82 \times 10^{20} B_\infty l^2 a n \quad (124)$$

Similarly, for strong Brownian motion or small velocity gradient,

$$\overline{F_{zz}} = \frac{7}{270} l^2 a B_\infty \beta (n^2 - 2n + 1) \left(1 + \frac{\alpha^2}{448}\right) \quad (125)$$

$$\frac{\eta_{sp}}{c} = \frac{\frac{k_B M_0}{1000\rho} + \frac{7\pi N}{45000} l^2 a B_\infty \beta \left(n - 2 + \frac{1}{n}\right) \left(1 + \frac{\alpha^2}{448}\right)}{1 - \frac{7\pi N}{45000} l^2 a B_\infty \beta \left(n - 2 + \frac{1}{n}\right) \left(1 + \frac{\alpha^2}{448}\right) c} \quad (126)$$

$$\approx 2.94 \times 10^{20} B_\infty l^2 a n \quad (127)$$

DISCUSSION

Although the chain molecules which have been considered in this paper have been purely hypothetical, consisting of single, like atoms linked together, there is nothing in the nature of the treatment which would not apply equally well to molecules consisting of *groups* of atoms linked together, provided, if random kinking is assumed, the interactions between these groups do not interfere with the randomness of the kinking and provided a suitable "effective radius" a for the group is used. One must count one group per joint (not one per repeating unit), and if all the groups are not alike, as in vinyl polymers, for instance, one must use some sort of average value for a .

It should be emphasized also that the derivations in this paper are based on the assumption that the contribution of each atom (or group) to the viscosity work is the same as if the flow of the immediately surrounding liquid were entirely unaffected by the presence of the neighboring atoms. This is, of course, untrue for actual chain molecules, in which the distance l between atoms or groups is not much larger (if at all) than the diameter of each. This may be corrected for by using for the *effective* radius, a , of an atomic group in a chain molecule a value somewhat smaller than its *true* radius. In the first paper of this series it was shown that approximate agreement with the empirical value for

the paraffins was obtained by assuming that a is the radius of a sphere having $\frac{1}{n}$ th the surface area of a cylinder having a length equal to n times

the length per CH_2 observed in solid paraffins and having the diameter required for molecular close-packing in the liquid state. No claim of accuracy or of theoretical validity is made for this method, however. Comparisons of empirically determined values of the effective radius for different series will probably lead to a better method of calculation.

It should be noted that the results for randomly kinked molecules differ from those for rod-like molecules in two important respects. *First*, they differ in their dependence on n , Staudinger's empirical relation (proportionality between η_{sp}/c and n) resulting only for kinked molecules. *Second*, they differ in their variation with the ratio q/T . This variation is negligible for randomly kinked molecules but very great for rod molecules.

SUMMARY

Theoretical derivations have been given for the previously reported general equation relating the viscosity of a dilute solution to the coordinates and sizes of the atoms in the component molecules, and also for the special equations applying to rigid chain molecules which are rod-like or are randomly kinked. The difficulty of determining theoretically the "effective radius" of a group of atoms in a chain molecule, for use in these equations, has been briefly discussed.

Long, randomly kinked chains should obey Staudinger's empirical "law." Long rod-like molecules should show a very great dependence of viscosity on the velocity gradient in the solution.

The assistance of Miss Dorothy Owen in making and checking many of the calculations for this paper is gratefully acknowledged.

REFERENCES

- (1) BOEDER, P.: Z. Physik **75**, 258 (1932).
- (2) EYRING, H.: Phys. Rev. **39**, 746 (1932).
- (3) DE HAAN, D. B.: Nouvelles Tables d'Intégrales Définies. P. Engels, Leide (1867).
- (4) HUGGINS, M. L.: J. Phys. Chem. **42**, 911 (1938).
- (5) KUHN, W.: Z. physik. Chem. **A161**, 1, 427 (1932).
- (6) KUHN, W.: Kolloid-Z. **68**, 2 (1934).
- (7) STAUDINGER, H.: Die hochmolekularen organischen Verbindungen. Julius Springer, Berlin (1932).

PLASTIC FLOW OF DISPERSIONS AND A NEW APPROACH TO THE STUDY OF PLASTICITY^{1,2}

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Plastic flow and plasticity are related. The former concerns the interdependence of stress and permanent deformation. The latter, as understood in practice and as defined by the dictionary, is the property through which the form of a mass can be readily changed or molded. In other words, a body has high plasticity if it can be greatly deformed without excessive rigid resistance. To define plasticity more exactly, it is necessary to possess a law of plastic flow, analogous to that of elastic flow. The measurement of plasticity on the basis of such a law and the analysis of the factors that determine plasticity constitute the subject matter of this work.

Examples of the substances considered are greases, fats, pastes of clay, lime, and cement, and cement mortars. These substances consist of a solid phase that is dispersed in a liquid to give a thick mass. We shall therefore refer to them as dispersions, but the sense of the word is wider than is customary in colloid chemistry, as coarse-size as well as colloid-size dispersoids are included.

At first glance it might appear that the definition of plasticity cited can not apply to dispersions, for the reason that rheologically these are liquids, not solids. Actually, however, dispersions of the kind considered possess rigidity, however small this may be in extreme cases. The origin of the rigidity is structure of the disperse phase, which is discussed in a separate section.

Owing to their solid character, dispersions interpose a resistance to plastic displacement of the elements of structure, which is the minimum resistance that must be overcome for continued deformation or plastic flow. In addition to the plastic resistance, there is a viscous resistance to be overcome, which increases with increase in rate of deformation but can theo-

¹ Presented before the Division of Colloid Chemistry at the Ninety-sixth Meeting of the American Chemical Society, held at Milwaukee, September, 1938. The subject matter was also presented before the 1135th Meeting of the Philosophical Society of Washington, April 23, 1938, and an abstract has been published (*J. Wash. Acad. Sci.* **28**, 384 (1938)).

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retically be reduced to zero by infinitely slow rate of deformation. Our interest in this work is solely in the fixed plastic component of resistance.

Plastic resistance is prominently encountered in the technical operations of shaping, molding, squeezing, and extrusion,—in fact, in all operations in which a change of form takes place. The change of form, or plastic flow, is calculated as a sum of infinitesimal displacements of an incompressible cylinder, down or up and outward, each equal to

$$dv = a \, dh + h \, da = 2a \, dh$$

where a is the area and h the height or thickness of the mass. The total plastic flow is $2\int_{h_0}^h a \, dh$. For the case in which all elements of the original volume partake of the complete displacement, the total plastic flow, by integration, is $\pm 4.605v_0 \log h_0/h$, where v_0 is the volume, a plus sign indicates compression, and a minus sign indicates tension.

This formula for extent of plastic flow is general. It can be made applicable to complex operations by figuratively replacing these by an equivalent simple operation of compression (very rarely, tension). Thus, extrusion of a mass of volume v_0 and of diameter d_0 through an orifice of diameter d can figuratively be carried out by compressing the mass in a succession of small steps in two alternate perpendicular directions until the diameter has been reduced to d , then slipping the reduced mass through the orifice. The total plastic flow is then given by twice (for two directions) the expression above, with d_0 and d replacing h_0 and h , respectively.

We have investigated the plasticity of dispersions as regards compressive stress. The question as regards other stresses is not considered; in the first place because the dispersions are not able to withstand any appreciable tensile or shearing stress, and in the second place because compression is the principal stress of technologic interest. Our results pertain to all operations with dispersions in which a compressive stress is perceived to enter.

Properties that differentiate dispersions of the kind enumerated are as follows: elastic limit is extremely small and there is no elastic after-effect; response to compressive stress is very rapid, and the final plastic deformation characteristic of the stress is ordinarily reached quickly.

A material may be soft as regards very small deformations, but may require much pressure for extensive deformation. The latter pressure we consider to be related to the property of plasticity. The distinction between mere softness and the plasticity of dispersions is illustrated by the following comparison between a clay paste and a paste of quartz powder. The former appears dry and stiff; the latter appears wet, and its softness is shown by the fact that it slumps under its own weight. It might from these observations be inferred that the quartz paste is more plastic than the clay paste. However, this is known not to be the case. The actual

higher plasticity of the clay paste is shown by the fact that it spreads out extensively with only moderately more stress required at the end than when spreading was commenced. In attempting to spread out the quartz paste, however, a very considerable resistance is experienced. If we attempt excessively to force the flow, the quartz paste ruptures.

It is very likely because of the tendency of a poorly plastic material to rupture during plastic flow that strength or cohesion is frequently made the measure of, or included in the definition of, plasticity. We should prefer, however, to define plasticity solely in terms of resistance to extensive deformation and to consider cohesion as a separate property. This separation of properties is logical, because even though cohesion and ease of deformation are more or less associated, as we shall see, nevertheless they are far from being in perfect relation to one another. It will be shown that it is possible for two substances to have nearly the same plasticity but a quite different cohesion.

The idea of measuring ease of deformation under load underlies innumerable devices for assessing plasticity. The most common of these is probably the familiar needle or rod which is allowed to penetrate a plastic mass. A different type of apparatus is the well-known flow table. Or, again, a mass is squeezed between two plates and the spread of the mass is noted. The principal defects of these devices are that they are not well defined for theoretical analysis and are arbitrary, as usually attention is focused on only one or two deformations, instead of all possible values. However, the approach is well founded, as ease of permanent deformation under stress is the measurement that is aimed at.

A second type of procedure, which has been applied particularly to clays, attempts to measure cohesion as a measure of plasticity. A plastic mass is compressed between two plates until cracks appear, or a string of material is extruded and the length of the broken piece measured, or a bar is twisted until it breaks. On the basis of a correct characterization of plasticity, the measurement of cohesion, while not without justification, is indirect and improper.

Even less direct are other methods that have been advanced, again particularly for clays. These include measurement of the amount, range, or retention of mixing water, the shrinkage, the dry strength, and the adsorption of water vapor or dyes. The basis of these procedures is the measurement of a property that varies more or less in the same manner as ease of deformation.

A method that has been widely followed in certain scientific circles comprises estimation of plasticity on the basis of results obtained from the measurement of viscous resistance. Bingham (1), who originated the procedure, concluded that the viscous flow of clay pastes through capillary tubes did not take place until a certain stress, the yield value, had been

exceeded, and that thereafter the shear-rate of shear curve was linear. However, Van Nieuwenburg (20) points out, in summary, that this ideal relationship is not true, but that the shear-rate of shear relation for dispersions is curvilinear (at least at the lower viscosities). Therefore the method of Bingham is impaired. More importantly, however, the method has faced serious difficulty in attempting to characterize the property of plasticity (cf. reference 2).

Fundamentally, the reason for the difficulty lies in the fact that basing plasticity on measurement of viscosity is wrong, because the wrong variables are used. Plasticity depends on actual deformation, not on rate of deformation or rate of shear. Therefore a technique based on measuring the rate of shear does not meet the issue and may be expected to be fruitless in promoting our knowledge of plasticity.

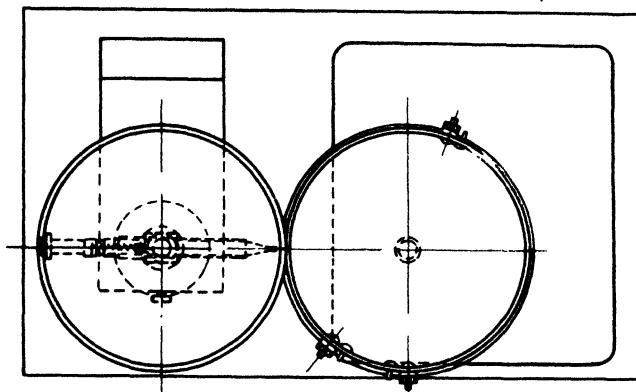
The complicated viscosity relationship for dispersions led McMillen (17) to emphasize the influence of thixotropy on the results obtained. This idea has recently been considerably advanced by Goodeve and Whitfield (11), who abandon altogether the unreal attempt to associate plasticity and viscous resistance. We may expect further development of the study of thixotropy (rather than plasticity) by viscosity measurement, insofar as the latter is not carried out as an end in itself.

In the present approach to plasticity based on measurement of deformation, differences in rate of deformation, or viscous effects, will affect the results for plasticity. However, our experience shows that the viscous effects are ordinarily small and may be neglected.

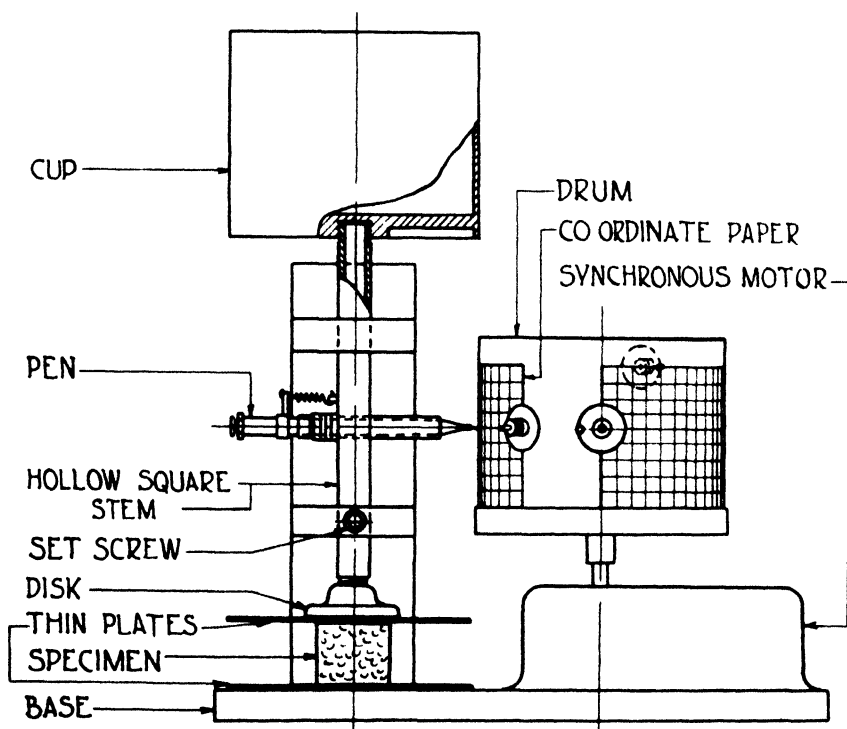
EXPERIMENTAL

Measurements were made of the continuous deformation of a cylinder of specimen while under a uniformly increasing compressive load. In the apparatus shown in figure 1 the stress is transmitted through a transmitting system, comprising a cup, stem, and disk, by fine lead shot flowing at a steady rate into the cup. As the cylinder of specimen, which consists of 20 to 60 g. of material, flows out plastically between the two thin plates between which it is completely contained throughout, a record is automatically made of the height of the cylinder on millimeter coordinate paper. For writing the record a fine ruling pen is used, which passes through a sleeve in the stem and is lightly held against the coordinate paper by a fine spring. The drum to which the paper is fastened is rotated by a self-starting synchronous clock motor. The rate of delivery of shot being known in terms of the linear movement of the paper, the record on the latter provides a relationship between height and load. To obtain a zero of reference, a fiduciary line is ruled on the coordinate paper with the disk of the transmitting system resting on the two thin plates.

To reduce the initial load on the specimen, the transmitting system was



TOP VIEW



FRONT VIEW

Scale - Cm

FIG. 1. The apparatus

made of laminated Bakelite and the square stem was hollowed out. Likewise the upper thin plate was made of Bakelite (the lower plate being of glass).

The metal tube through which the lead shot flowed was electrically vibrated to promote evenness of flow, which was tested for. At the end of each experiment the cup and its content of shot were weighed to determine exactly the rate of flow of shot. The shot was delivered through a glass nozzle, the end of which fitted into a rubber-hose connection and was flared.

All powders were in the air-dry state. In the preparation of pastes and mortars, troweling with a spatula was carried out for 2 min., after wetting by the added liquid. The quantity of liquid is given in percentage, which is equal to cubic centimeters per 100 g. of solid.

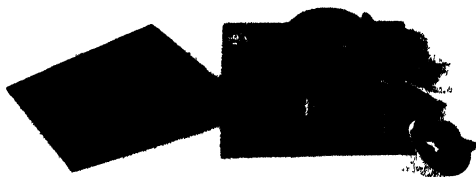


FIG. 2. Mold and parts

Specimens were molded in the apparatus shown in figure 2. The cylindrical mold, which had a taper of 1 in 20, was tightly held by flat springs to a smooth Bakelite base (to minimize loss of liquid in the mix). After all contact surfaces were thinly oiled, the material was added to the mold with squeezing and puddling so as to fill the mold completely and to avoid as much as possible entrainment of air bubbles. After the mold was filled, the base was tapped a few times against the table top to consolidate the mass. The springs holding down the mold were released and pushed aside, and the top of the mold was leveled off with a spatula. The inverted mold, which rested on the glass plate, was carefully lifted away from the specimen with the aid of the retaining disk shown in figure 2, and the disk was slightly twisted and slid off the specimen. Manipulation, or shearing if necessary, with a glass fiber was often useful in the latter operation.

The finished specimen naturally was not a perfect cylinder. This im-

perfection was one of the errors of the experiment which will be considered. At times the finished specimen slumped markedly under its own weight. However, the initial height of the specimen was necessarily taken to be the height of the mold, while the initial diameter was taken to be the mean diameter of the mold.

In beginning an experiment, the specimen resting on the glass plate was transferred to the apparatus, carefully centered beneath the disk of the transmitting system, the oiled Bakelite plate placed on the upper surface of the specimen, and the loading system carefully brought to rest on the specimen after releasing the set screw. With the electric vibrator turned on, the flow of shot and rotation of the drum were started simultaneously. The loading time was 4 min. or less under the usually preferred condition of a rate of shot of 1000 g. per minute, a diameter of specimen of about 28 mm., and a height of about 25 mm. (the preferred rate for petrolatum and

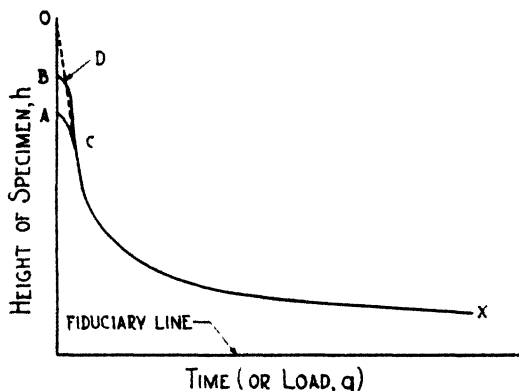


FIG. 3. Normal type of experimental curve

lanolin was less, and the preferred specimen for mortars was wider in proportion to its height). The initial load in our experiments was by direct measurement 110 g., while the final weight totaled up to 4000 g.

EXPERIMENTAL DEFORMATION CURVES

The normal type of curve obtained experimentally is shown in figure 3, in which the ordinate is the height of specimen and the abscissa the time of continuous loading. The rate of loading being known, the time is equivalent to the load.

The vertical distance OA or OB represents the initial decrease in height of the specimen from its original height. The initial decrease is due to the initial load, which consists of half the weight of the specimen plus the weight of the transmission system. The initial decrease is quickly attained and ordinarily does not vary with the time. As loading proceeds,

the height of the specimen follows hyperbolically along ACX or $BDCX$. Were there no initial load, the curve would follow along $ODCX$.

If one plots, as shown in figure 4, $\log h$ against $\log g$, where h is the height of specimen and g the load, a straight line is obtained over a more or less wide range. From this line one may calculate the constants of plastic flow. The curvilinear parts AC and BDC of the plot, occurring at small loads, represent partly unavoidable experimental deviations, which we shall call, respectively, type I and type II initial deviations. Type I deviation is due to the effect of the initial load. Owing to the initial load being static, it causes a greater deformation than the same load dynamically applied, as will be seen later. Type II deviation is also due partly to the effect of the initial load (portion BD) but primarily to entrained air bubbles (portion DC). These air bubbles cause the specimen to appear

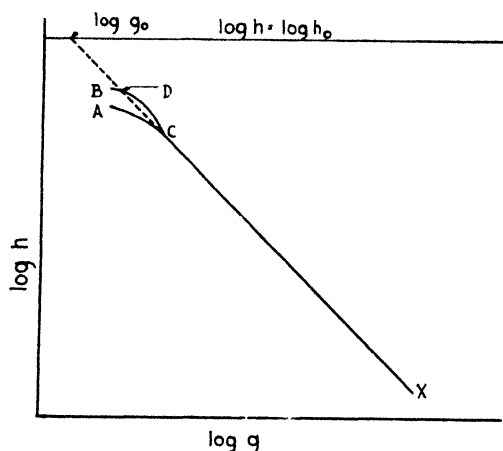


FIG. 4. Plot for determining constants of plastic flow

relatively tall near the beginning compared to later when they have been substantially squeezed out or flattened out, so that as a result portion DC of the initial deviation lies above the extrapolated $\log h$ - $\log g$ line of figure 4.

Type I deviation usually occurs in the case of fairly fluid dispersions, such as pastes containing much added liquid, and in the case of comparatively non-plastic dispersions such as mortar. Type II deviation usually occurs for thick materials such as grease or fairly stiff clay pastes that tend to occlude air, which occlusion is indeed observable to the eye.

The extent of deviation AC or BDC is variable; in general, it is greater the stiffer the material, that is, the less it flows plastically under a given maximum load. When the dispersion is quite stiff, as when the amount of liquid is small, the initial deviation may constitute almost all of the ob-

served plastic flow. In this case it will be virtually impossible to decide which of the experimental points should be included in the linear part of the $\log h$ - $\log g$ plot, and which should be neglected as belonging to the initial deviation. To answer this question one of two expedients may be followed. The first is to increase the total deformation, either by increasing the rate of loading and thus the total load or by decreasing the cross-sectional area of the specimen. This is the only expedient when the dispersion is fixed. On the other hand, if the dispersion is prepared, as when a liquid is added to a powder, uncertainty as to the initial deviation in the case of too stiff a paste may be overcome in a second way, by plotting the curve for other, more fluid, pastes of the same powder. The principle is then applied that the $\log h$ - $\log g$ lines are parallel for different dispersions of the same solid and liquid. In the case of the more fluid pastes, the initial deviation is relatively small and easily corrected for, so that the resulting linear $\log h$ - $\log g$ plot serves as a good guide for the plot for the stiffest pastes. A series of such dispersions of the same material is usually necessary in evaluating plastic constants of poorly plastic materials such as mortars.

Other types of experimental deformation curves, less generally encountered, are shown in figure 5. Discontinuous plastic flow is characterized by flow taking place in slips, each of which follows a period of non-flow with increasing stress. The aqueous paste of hydrated lime provided an outstanding example. Discontinuous flow as a rule was exhibited by lyophobic dispersions (which are ordinarily thixotropic), such as quartz or calcium carbonate dispersed in kerosene, or calcium carbonate dispersed in aqueous sodium oleate solution.

In the case of discontinuous plastic flow, if one considers the height of specimen and the load at a point immediately following a slip, the same linearity of the $\log h$ - $\log g$ plot is obtained as for continuous flow. The dotted curve of figure 5 shows the curve of continuous flow that is equivalent to that of discontinuous flow.

Elements of discontinuous flow are occasionally interspersed in continuous flow, particularly at the smaller deformations. This peculiarity for a given solid phase is most noticeable for the more fluid pastes and tends to disappear when the paste is stiffer. Ball clay (English) provided an outstanding example of partial discontinuous flow. When the rate of stress was greatly decreased, the partly discontinuous curve for the ball clay became a quite discontinuous curve.

As for the discontinuous-flow curve, experimental points of the partly discontinuous curve taken immediately after slip give a straight line in the $\log h$ - $\log g$ plot. Near a discontinuity no experimental points other than those immediately following the slip should be considered.

A second abnormal type of plastic-flow curve is that in which the flow

suspends after a certain extent of deformation. This type of curve was given by Portland cement paste and by the less plastic pastes of non-plastic kaolin and silica when they contained a large excess of mixing water. Naturally only the flow part of the curve can be used in calculating the plastic flow constants, but a reservation should be made as to the type of flow.

Finally, a type of curve has been encountered in which the cylinder of material fails mechanically during flow. The failure is characteristic of

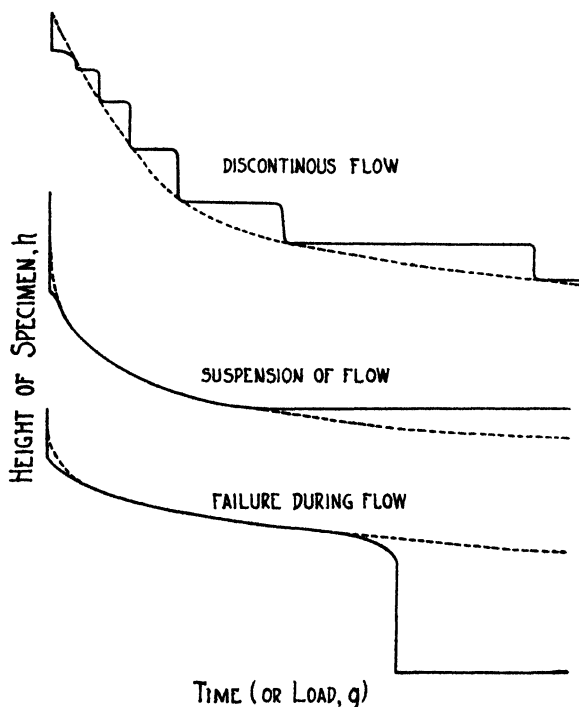


FIG. 5. Abnormal types of experimental curve

cement mortars, which are among the least plastic and least cohesive of any of the materials considered.

It will be observed in comparing the top and bottom curves of figure 5 that a resemblance exists between discontinuous and failing flow. If the latter is accompanied by a period of discontinuous flow preceding failure, some difficulty may be experienced in distinguishing the type of curve. In such a rare instance the answer will be found in the physical character of the dispersion.

We now consider briefly the precision of fit in a linear $\log h$ - $\log g$ plot. Values of h were read from the experimentally obtained curve of plastic

deformation to ± 0.1 mm. with the aid of a magnifying glass. In plotting a curve, a set of values of h corresponding to approximately equal intervals of $\log g$ was taken. Data are given in table 1 for typical dispersions. The values of $\log h$ in parentheses belong to the initial deviation and so were not considered in determining the linear plot. A minus sign indicates that the deviation is of type I, and a plus sign that it is of type II. Discontinuous flow is represented by hydrated lime, suspension of flow by Portland cement, and failure during flow by the cement mortars. Parentheses in the case of Portland cement surround values belonging to the region of suspended flow.

The precision of fit was estimated by noting the deviation, $\Delta \log h$, between the experimental values of $\log h$ and the corresponding values taken from the best straight line through the points. The deviations are seen to be plus and minus at random. The average deviation varied from ± 0.1 to ± 1.5 per cent and for many typical specimens was ± 0.6 per cent.

LAW OF PLASTIC FLOW

The law underlying the observed linearity in a plot of $\log h$ against $\log g$ may be expressed as follows:

$$\kappa = \frac{dp/p}{dv/v_0} \quad (1)$$

In this equation p is the applied compressive stress, v_0 the volume of specimen, and dv the differential volume of plastic flow corresponding to an increment of pressure, dp . κ is a dimensionless constant which measures the rate of increase in plastic resistance accompanying continued plastic flow. κ has therefore been called the coefficient of renitence (from *renitens* = resistant).

Since

$$dv = -2v_0 \frac{dh}{h}$$

equation 1 may be written (overlooking the factor 2)

$$\kappa = \frac{dp/p}{dh/h} \quad (2)$$

Integration leads to the relation

$$\kappa = \frac{\log p/p_0}{\log h_0/h} \quad (3)$$

In equation 3 h_0 is the initial height of specimen (height of the mold in which it is formed). Constant p_0 is evidently the pressure which must

just be exceeded for plastic flow to commence; therefore p_0 is properly called the yield value. Frequently one-half the weight of the specimen itself is greater than p_0 , and the mass therefore slumps as soon as it is removed from the mold.

κ and p_0 in equation 3 are the two fundamental constants of plastic flow of a dispersion.

As load g is the experimental variable, it is desirable to determine the plastic flow constants directly in terms of g and h instead of p and h . This may be done by a simple transformation of equation 3. Since g is equal to pa , and ah is equal to a_0h_0 , the following relation holds:

$$\log p/p_0 = \log g/g_0 + \log h/h_0 \quad (4)$$

Substituting from equation 4 into equation 3 we obtain

$$\kappa + 1 = \frac{\log g/g_0}{\log h_0/h} \quad (5)$$

Equation 5 furnishes the basis for experimental determination of the plastic flow constants of a material. The negative slope of the straight line obtained in a plot of $\log h$ against $\log g$ is equal to $\kappa + 1$. Constant g_0 is obtained, as shown in figure 4, by extrapolating the straight line back to its intersection with $\log h = \log h_0$ (or the intersection may be determined by calculation). Yield value p_0 is given by the ratio g_0/a_0 , where a_0 is the initial mean area of the specimen. Instead of g , one may employ p calculated from point to point. The same results are obtained for κ and p_0 , only more laboriously.

The precision of the plastic flow constants themselves naturally will be less than the precision of fit in a $\log h$ - $\log g$ plot. The additional errors are due to inaccuracy in preparing the specimen, to variation of temperature, and to effects of the initial deviation.

Separate determinations of the plastic flow constants were made over a period of many months. For typical materials the average deviation in κ ranged from ± 1.5 per cent to ± 10.2 per cent, averaging ± 4.9 per cent, and in p_0 from ± 4.2 per cent to ± 11.7 per cent, averaging ± 7.3 per cent. Much of the deviation obviously was due to fluctuation of temperature, which ranged from 25° to 30°C.

PROPORTION OF PHASES, LIQUID RETENTION, AND STANDARD YIELD VALUE

The coefficient of renitence, κ , is significantly independent of the proportion of the phases. This is shown by the parallelism of the different $\log h$ - $\log g$ lines for dispersions of a given solid phase with different percentages of the same liquid. In a few cases the best straight lines of the $\log h$ - $\log g$ plot could not be drawn quite parallel. The deviation

was small, however, and was most probably due to experimental error, so the values of κ were averaged to give a value characteristic of the system.

Yield value, p_0 , decreases, it is found, with increase in percentage of liquid in the dispersion, as is to be expected. Moreover, a definite relationship holds between yield value and liquid content, as shown in figure 6, where a straight line is seen to be obtained when $\log p_0$ is plotted against

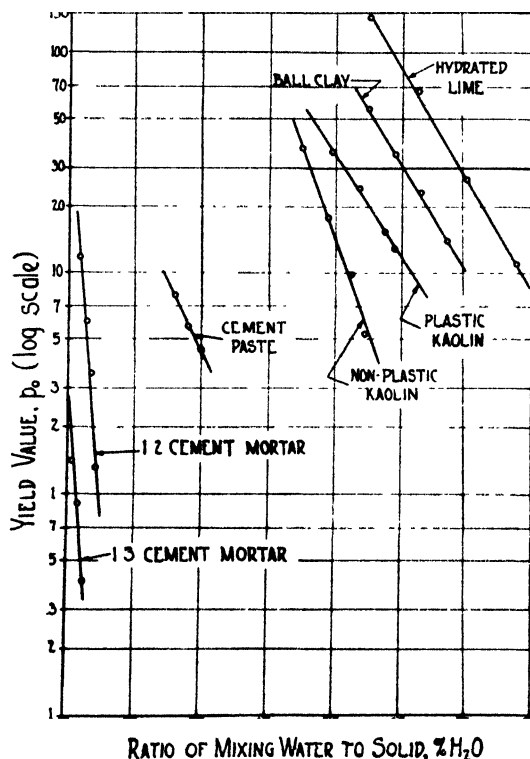


FIG. 6. Showing the linear relationship between $\log p_0$ and w

w , the percentage of mixing liquid (expressed as cubic centimeters per 100 g. of solid). The relationship may be written

$$p_0 = \alpha e^{-\beta w} \quad (6)$$

The closeness with which equation 6 is obeyed is given by the mean deviation in w , which ranged from ± 0.2 per cent to ± 1.0 per cent, and, for typical systems, averaged ± 0.6 per cent.

A characteristic property of a dispersion is the volume of liquid that is necessary to bring it to a practicable consistence. The liquid thus re-

quired is often referred to as the liquid retention. We shall define liquid retention, *L.R.*, quantitatively as the percentage of liquid that is retained by a dispersion at a specified yield value of reference. The latter, as indicated by the data of figure 6, is conveniently chosen as 10 g. per square centimeter.

The reciprocal of *L.R.*, or the yield value at a given percentage of liquid phase (unspecified in this paper), may be called standard yield value. A large standard yield value implies a large value of *L.R.*, and *vice versa*.

RELATION OF CONSTANTS TO SOFTNESS, PLASTICITY, WORKABILITY, AND COHESION

A number of adjectives are commonly employed to describe the character of a dispersion. These may be given quantitative significance by means of their relation to the constants of plastic flow.

One changes the consistence of a dispersion by change in its liquid content, making it softer by increase and stiffer by decrease in the proportion of liquid. Likewise, constant p_0 varies with the proportion of liquid, and, moreover, being the yield value, it is also a measure of the stress required for very small deformations. Therefore consistence, softness, and stiffness are qualitative aspects of p_0 , consistence being the general term, "soft" signifying low yield value, and "stiff" high yield value.

Plasticity and renitence refer to the plastic resistance to large deformation. A dispersion that is plastic requires little stress for extensive plastic flow, but one that is renitent requires much stress. In what follows it is demonstrated that constant κ is an inverse quantitative measure of plasticity (and, conversely, a direct measure of renitence).

Equation 3 may be written in the following form:³

$$p = p_0 \left(\frac{h}{h_0} \right)^\kappa \quad (7)$$

Equation 7 shows that the stress increases exponentially with the degree of deformation. Both p_0 and κ are parameters of the equation, but since κ is the exponent, it is of prime importance in determining the stress at large deformations. In fact, regardless of the value of p_0 , the dispersion with the greater value of κ will eventually require the greater stress for a sufficiently large deformation. The origin of κ as an inverse measure of plasticity is therefore proved formally.

The same conclusion as to the significance of κ is arrived at by practical

* After this study of dispersions had been completed and equation 7 discovered, the writer learned of a paper by Bogomolova and Kunin (3), in which the same equation was found to express the plastic flow of polycrystalline lead in compression. The exponent had the same magnitude whether the stress was applied slowly or suddenly.

test. The fixed organic dispersions of table 2, and the prepared pastes of clay and lime of table 3, all had a value of κ of about 1 or less. On the other hand, κ was much larger for the patently less plastic materials.

TABLE 2
*Plastic flow constants of organic disperse substances**

DISPERSION	κ	p_0
Lanolin, anhydrous.....	1.30 ± 0.02	0.42 ± 0.03
Petrolatum.....	0.44 ± 0.02	1.44 ± 0.12
Cold cream.....	0.94 ± 0.04	1.70 ± 0.2
Cup grease.....	0.80 ± 0.02	5.4 ± 0.4
Shortening.....	0.61 ± 0.03	12.6 ± 0.8
Fiber grease.....	0.59 ± 0.06	25.9 ± 1.1

* κ = coefficient of renitence; p_0 = yield value in grams per square centimeter.

TABLE 3
*Plastic flow constants of aqueous pastes and mortars**

DISPERSION	κ	L.R.	SEDIMENTA- TION VOL- UME	p_0			
		per cent	cc. per gram	grams per square centimeter			
Hydrated lime.....	0.63	83.1	3.7 ± 0.1	10.9 _{82.5}	26.2 _{75.0}	65.7 _{67.5}	148.0 _{60.0}
Dolomitic hydrated lime...	1.24	78.0	2.9 ± 0.1	3.9 _{90.0}	6.6 _{32.5}	13.6 _{75.0}	
Dark ball clay.....	0.97	75.4	2.4 ± 0.0 †	13.8 _{72.0}	22.8 _{68.0}	34.0 _{64.0}	52.2 _{60.0}
Light ball clay....	0.82	69.4	2.5 ± 0.1 †	8.3 _{72.0}	12.0 _{68.0}	16.0 _{64.0}	
Plastic kaolin.	0.93	66.1	3.1 ± 0.1	12.7 _{64.0}	15.2 _{62.5}	24.0 _{68.5}	35.1 _{64.5}
Non-plastic kaolin.	2.4	56.3	1.6 ± 0.0	4.5 _{60.0}	9.8 _{57.0}	14.9 _{64.0}	32.3 _{60.0}
Crystallized cal- cium carbonate..	6.9	47.3	1.1 ± 0.0	0.012 _{56.7}	0.20 _{58.3}	1.57 _{60.0}	
Quartz powder....	10.4	28.4	0.8 ± 0.0	0.0020 _{21.7}	0.020 _{50.8}	0.043 _{30.0}	
Portland cement..	1.17	29.2	1.0 ± 0.0	4.5 _{55.0}	5.7 _{55.0}	7.9 _{51.0}	
1:2 cement mortar.	6.3	17.0		1.3 _{19.3}	3.5 _{18.4}	6.0 _{17.6}	11.7 _{16.7}
1:2.6 cement mor- tar.....	22	14.9		0.3 _{18.6}	0.8 _{17.8}	1.4 _{17.0}	
1:3 cement mortar.	38	13.6		0.4 _{17.5}	0.9 _{16.7}	1.4 _{15.8}	

* κ = coefficient of renitence; L.R. = liquid retention; p_0 = yield value (subscript is percentage of mixing water).

† The low value is due to incomplete deflocculation of the clay.

It was 2.4 for non-plastic kaolin, 6.9 for the less plastic calcium carbonate paste, and 10.4 for the obviously still less plastic quartz paste (table 3). In the case of cement mortar, κ increased from 6.3 for the mortar contain-

ing least sand to 38 for the much less plastic mortar containing most sand.

With κ less than about 1, qualitative differences in plasticity could not be detected. However, there is no reason to suspect that the meaning of κ is essentially any different here than at the higher values of κ . Thus, empirical test with the Emley plasticimeter (made by J. E. Conley of this Station) and other indications revealed that the dolomitic lime was much less plastic than the hydrated (high calcium) lime, which is in agreement with a value for κ of 1.24 for the former and of only 0.63 for the latter.

The smaller κ is, the greater by equation 7 is the initial range of deformations over which the magnitude of p_0 has a significant bearing on the stress. As a result, when κ is less than about 1, a prominent characteristic of dispersions is their softness or stiffness. Thus the stiffness of the fixed dispersions of table 2 increased in the order given, which is also the order of increasing p_0 . However, as p_0 for these dispersions could be arbitrarily varied, the order is adventitious. Therefore, regardless of the consistence, one compares the inherent property of plasticity, and notes that fiber grease with κ equal to 0.59 is more plastic than cup grease with κ equal to 0.80, while lanolin with κ equal to 1.30, in spite of its considerable softness, is least plastic of all, as was indicated by its comparatively "tough" reaction to pressure. Such comparisons of κ , however, should not minimize the importance of correct adjustment of p_0 for any material.

When κ is zero, a stress equal to the yield value will cause plastic flow to continue indefinitely. We then obtain the perfectly plastic substance referred to by Nadai (19). No such substance has been observed in this study, the smallest value of κ being 0.44 for petrolatum.

Consistence and plasticity are contributory properties; workability, however, is an ultimate property which determines the feasibility of operating with a dispersion. Workability is compounded of consistence and plasticity. In order for a dispersion to be workable, it must be both sufficiently soft and plastic. For example, regardless of high plasticity of the system clay-water, in order for it to work properly it must be softened by the addition of sufficient water. Furthermore, the dispersion must be sufficiently plastic, else the stresses that are built up during plastic deformation will be excessive, either taxing the operator or causing rupture of the material, or both.

However, p_0 and κ are not of equal value in determining workability. Because of its exponential character, κ is of generally greater significance in determining the stress at practical deformations, although the particular magnitude of p_0 may carry considerable weight. Beyond this, however, p_0 is readily altered by a mere change in proportion of the phases, whereas κ cannot be changed without changing the character of the

TABLE 4
Test of factors determining plasticity and cohesion*

DISPERSION	α	L.R. per cent	SEDIMENTA- TION VOL- UME cc. per gram	p_0 grams per square centimeter	
Calcium carbonate and water.....	6.9 \pm 0.6	47.3	1.18	0.012 _{14.7}	1.57 _{10.0}
Calcium carbonate and 0.1% sodium oleate solu- tion.....	3.8	49.6	1.52	0.50 _{14.7}	9.2 _{10.0}
Calcium carbonate and kerosene.....	2.7	70.0	1.76	6.9 _{73.3}	23.8 _{13.7}
Calcium carbonate and 0.1% oleic acid in kero- sene.....			1.12		
Calcium carbonate and 0.0025 M calcium chlo- ride.....	5.8 \pm 0.9	48.5	1.14	0.22 _{14.7}	3.6 _{10.0}
Quartz and water.....	10.4	28.4	0.80	0.0020 _{11.7}	0.043 _{10.0}
Quartz and 0.1% sodium oleate solution	11.3	26.4	0.74	0.00013 _{10.0}	0.0021 _{13.7}
Quartz and kerosene.....	2.4 \pm 0.2	32.5	1.32	0.58 _{14.3}	3.4 _{14.7}
Quartz and 0.1% oleic acid in kerosene.....	1.3 \pm 0.2	30.5	1.26	0.52 _{14.3}	1.91 _{10.7}
Quartz and 0.050 M calcium chloride	8.2	29.4	0.87	0.088 _{11.7}	2.6 _{10.0}
Light ball clay (unground) and water.....	1.08 _{10.0} 0.93 _{13.3} 0.91 _{14.7}	52.2	2.5†	2.2 ₁₀	23.0 _{14.7}
Light ball clay (unground) and 0.050 N sodium hydroxide.....	0.87 _{10.0} 0.79 _{13.3} 0.60 _{14.7}	55.5	3.9†	4.6 ₁₀	49.5 _{14.7}
Light ball clay (unground) and 0.050 N hydro- chloric acid.....	0.95 _{10.0} 0.76 _{13.3} 0.69 _{14.7}	53.7	2.7†	3.5 ₁₀	35.6 _{14.7}

* α = coefficient of renitence; L.R. = liquid retention; p_0 = yield value (subscript is percentage of mixing water).

† Measurement on finely ground clay.

system. Therefore, κ , or plasticity, is fundamental, while p_0 , or consistence, is incidental.

Having considered κ and p_0 , we now consider the relations and significance of $L.R.$ The data in tables 3 and 4, when plotted as in figure 7, show that κ and $L.R.$ vary in the same way (the correlation coefficient between $\log \kappa$ and $L.R.$ was -0.76). This result agrees with a well-known empiricism to the effect that the greater the liquid retention, the greater the plasticity.

As indicated, the relation between $L.R.$ and κ is not uniform; two substances may have equal values of κ but quite different values of $L.R.$ Investigation of such irregular cases leads to the conclusion that $L.R.$

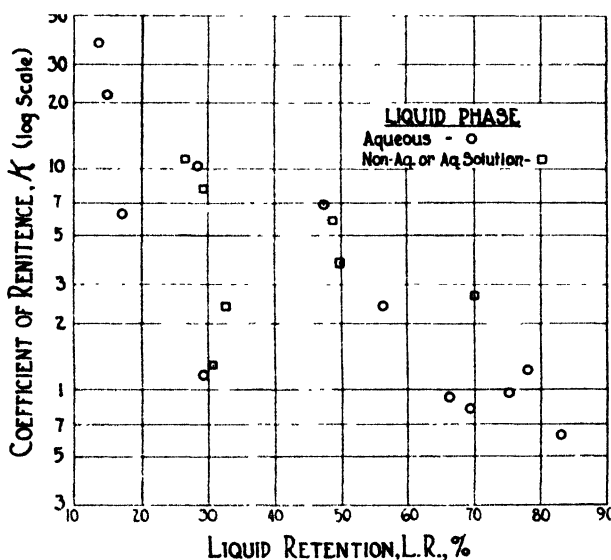


FIG. 7. Showing that a relation exists between $L.R.$ and κ

is a measure of cohesion, or, by equivalence, of elongation, or resistance to rupture; also of stickiness, as a cohesive dispersion is as a rule also sticky. This conclusion is demonstrated in the comparisons that follow.

Cohesion of a paste was estimated crudely, but as two or more pastes were compared at one time and as only large differences were considered, the procedure was sufficient. Observations were made as to whether the mass clung together or tended to break up into small masses; the traction, and the amount and outward extension of the material adhering to a spatula or glass rod, were also observed.

It was soon learned that $L.R.$ could be compared only for dispersions for which κ was about the same, so this procedure was followed. Quartz powder made up with a solution of 0.1 per cent oleic acid in kerosene,

Portland cement paste, and the paste of dolomitic lime hydrate all had nearly the same value of κ ,—about 1.2 (tables 3 and 4),—and accordingly they were all plastic. However, *L.R.* was unusually low for two of the three, being, respectively, 30.5 per cent, 29.2 per cent, and 78.0 per cent. It was easy to see that, corresponding to its relatively high *L.R.*, the dolomitic lime had a much higher cohesion and stickiness than either of the two other dispersions. Attention should be drawn particularly to the quartz dispersion, which was “smooth” and “buttery,” as would be expected from its low value of κ ; at the same time, however, a poor cohesion, or brittleness, corresponding to the relatively low *L.R.*, was apparent. In other words, the quartz dispersion could be worked satisfactorily but only with great care.

The paste of calcium carbonate and water, and the 1:2 cement mortar, also had about the same value of κ , about 6.5. However, *L.R.* for the calcium carbonate was 47.3 per cent, but for the mortar only 17.0 per cent. Corresponding to its lower *L.R.*, the mortar was less cohesive, as shown not only by its behavior directly, but also by the fact that it failed mechanically during test, whereas the calcium carbonate paste did not.

Dispersions of calcium carbonate and of quartz in kerosene had about the same value for κ , namely, about 2.5. *L.R.* for the carbonate was 70.0 per cent, but for the quartz only 32.5 per cent (table 4). The corresponding greater cohesion of the calcium carbonate was easily apparent.

With *L.R.* at 70.0 per cent, the dispersion of calcium carbonate in kerosene might have been expected, were *L.R.* alone considered, to show as much cohesion as the clays or plastic kaolin of table 3. Actually it was much less cohesive. To explain this it will be noticed that κ for the calcium carbonate was 2.7, whereas for the clays and kaolin it was less than 1. This result indicates the importance of making comparison at approximately equal values of κ . It shows also that a given value of *L.R.* will represent a smaller cohesion the greater the value of κ .

It was ascertained that dark ball clay (table 3) was more cohesive than light ball clay, and that this in turn was more cohesive than the plastic kaolin. The values of κ being about the same, the differences are explained, as usual, by the respectively decreasing values of *L.R.* However, hydrated lime, contrary to what would be expected from its low κ and high *L.R.*, had an apparent cohesion more like the plastic kaolin than like the ball clays. Pending further investigation, this deviation may be attributed to the fact that the lime exhibited discontinuous plastic flow, whereas the clays and kaolin exhibited essentially continuous flow. Naturally a difference in the type of flow will affect comparison when this is close.

From the experimental results the following conclusion, subject to effects due to type of flow when comparison is close, appears to be justi-

fied, namely, that *L.R.* is a measure of the cohesion or stickiness of a dispersion, provided that comparison is made at approximately equal values of κ . The higher *L.R.* is, the greater is the cohesion.

It is to be noted that the dispersions that exhibited the anomaly of a low κ and a low, instead of a high, *L.R.* (quartz with a solution of oleic acid in kerosene and Portland cement with water) were those in which the solid phase was coarsely divided. It appears therefore that while, by proper choice of liquid phase, a coarsely divided solid phase may be made to yield a dispersion that is plastic, it will not yield one that is at the same time cohesive. Cohesion appears therefore to be peculiarly a function of particle size, that is, of dispersity of the solid phase, and a high cohesion appears to require a finely divided solid phase.

A property observed to be related to *L.R.* was the specific volume of the mass. Dispersions with high *L.R.* gave relatively voluminous masses, and *vice versa*. The correlation is understandable when one remembers that by definition *L.R.* represents simply the volume of liquid per unit weight of solid, so that a high *L.R.* would be expected to result in a dispersion of high specific volume.

THEORY OF PLASTIC FLOW OF DISPERSIONS

A theory of plastic flow has been developed that is based on consideration of the structure of the disperse phase, the process of plastic flow, and the nature and effect of the forces acting between the particles of disperse phase. Deductions based on the theory have been found very satisfactory in explaining results obtained and in predicting plasticity.

A schematic representation of the disperse structure before plastic flow has taken place is shown in figure 8 (a), in which for simplicity the particles are regarded as rectangular parallelpipeds. The structure is the same as that usually considered to describe the flocculated state. The structure is held together by the forces of attraction between the particles of disperse phase, and these forces of attraction are responsible for the rigidity of the dispersion. The attraction occurs in a random way mainly at corners and edges.

Initial rigidity, or yield value, is determined by the sum total force of attraction between the particles at the initial mean distance of separation of the particles corresponding to the arbitrary proportion of liquid. When the percentage of liquid phase is increased, the distance of separation is increased. This results in decrease in total force of attraction and hence a decrease in yield value, as observed.

Standard yield value, like yield value, is determined by the sum total force of attraction, but at a specified liquid content of reference. Since *L.R.* (liquid retention) varies proportionately with standard yield value,

it may be considered to be determined also by the total force of attraction at a given liquid content of reference.

During plastic flow we conceive that the initial configuration a of figure 8 changes over into configuration b.⁴ The latter configuration differs from the initial one in two respects. In the first place the particles of disperse phase are forced relatively close together in the direction of the unilateral stress. This is indicated in the case of coarse dispersions by the well-known laminated structure of impurities and of air bubbles in plastically compressed pastes. In the case of colloidal dispersions it is shown by the Brewster effect, or double refraction induced in an amorphous mixture squeezed between two plates, an effect which is interpreted (5) as resulting from the molecules (colloid particles) being forced relatively close together in the direction of the compressive stress; moreover

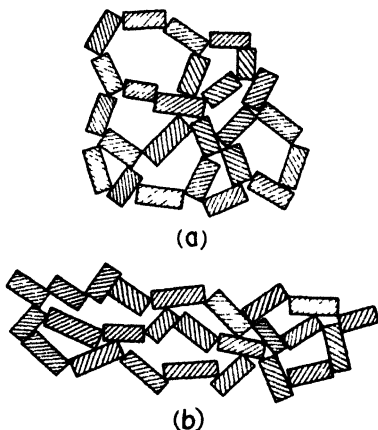


FIG. 8. Schematic representation of structure of dispersion: (a) before plastic flow and (b) after plastic flow.

it is indicated by the lenticular shape (14) taken on by air bubbles in gelatin that has been plastically deformed in compression.

In the second place, structure b differs from structure a in that the

⁴ It is the excess free space associated with the flocculated state that makes plastic flow at all possible. If the particles were densely packed, they could not slip past one another during application of unilateral stress, and there would be no plastic flow. Dense packing is considered to be the condition of suspension of flow.

Permanence of the deformation implies that the bonds are completely broken during plastic flow and new ones are formed. If the bonds were to retain their identity and were merely stretched, as one would expect for molecular bonds, elastic flow, or elastic after-effect, would be observed.

The weakness of the bonds and consequent low activation energy explains the observed extremely rapid yielding of dispersions under stress to a final state characteristic of the stress.

particles of disperse phase, owing to their flow, and by slipping, rolling, and rotating (18), contact each other more and more at their faces, rather than at corners and edges, and therefore over a greater surface.

As a result of the particles of disperse phase approaching closer to one another and contacting each other over a greater area, the total force of attraction increases. This explains the increasing resistance to continued plastic flow.

The greater the specific force of attraction, or the force at unit distance of separation of the particles, the more intrinsically stable the structure is, and the more therefore it retains its original configuration during plastic flow. The rate of increase of plastic resistance with increase in the extent of flow is correspondingly small. The rate, however, is measured by κ , so that κ may be considered to be determined by the total force of attraction at unit distance of separation of the particles of disperse phase. This interpretation of κ fits in with the fact that it is independent of the proportioning of the phases.

It is now observed why κ and $L.R.$ both vary in the same way in general, though not in detail. Each increases with increase in the sum total force of attraction, but under somewhat different conditions: in the case of κ , it is the force at unit distance of separation that counts, while in the case of $L.R.$, it is the force at a certain liquid content of reference.

Cohesion may, by its definition, be considered to depend substantially on the same condition as does $L.R.$, so that the relation between them is thereby understood. However, in order that comparison as to cohesion be valid, it is necessary that the stresses during extensive deformation be similar. This condition is essentially realized when κ is the same for the substances being compared.

The exponential variation of p_0 with w by equation 6 implies that the distance of separation of the particles, or pore size, also varies exponentially with the percentage of liquid phase. The same result has been obtained in a quite different way by Clews, Macey, and Rigby (8); according to them the flow conductivity of water through clay pastes, and hence the pore size, increase exponentially with the amount of water in the paste. In contrast to these results, one would in general expect a simple algebraic variation. This implies, however, constant density of liquid. The exponential variation may be due to a decrease in density of the liquid phase with increase in size of the pores, by analogy with the dynamical result that the internal pressure of a drop, and hence the density, vary inversely with the radius.

Having explained theoretically the significance and interrelations of p_0 , κ , and $L.R.$, it remains to test the theory in detail. This may be done by varying the factors that determine the sum total force of attraction between the particles of disperse phase, and observing the concomitant

change in plasticity and cohesion. The factors are (1) intrinsic attractive force, (2) electrokinetic potential, (3) solvation, (4) dispersity, and (5) particle shape.

As a direct indication of changes in attractive force, sedimentation volume was made use of. Ehrenberg (9) pointed out that sedimentation volume is large when the attraction between the particles of a settled suspension is great, because the particles are then united into spacious agglomerates; on the contrary, sedimentation volume is small when the attraction is small because the particles then slide past one another into a densely settled mass. von Buzagh (6) demonstrated this hypothesis by comparing the adhesion of quartz particles to a quartz surface with the sedimentation volume in different liquids.

Sedimentation volume was determined in a 10-cc. glass-stoppered cylinder, using 2 g. of fine powder or 5 g. of coarse. The liquid was added *in vacuo*, the lumped powder stirred up with a glass rod, the cylinder filled to the brim with liquid, and the suspension vigorously shaken and allowed to settle.

(1) *Intrinsic attractive force.* The intrinsic force of attraction operative between the dispersed particles is probably of the London-van der Waals (4, 12, 15) type. Bradley (4) and Tomlinson (22) find that the attraction between small spheres increases linearly with the diameter of the sphere, as the theory requires. Bradley (4) and Hamaker (12) have calculated for spheres that the London-van der Waals force varies inversely as the square of the distance of separation; in other words, the London-van der Waals force is analogous to that of gravitation.

A difference in intrinsic attraction probably explains, in the main, differences in plasticity of the dispersions of calcium carbonate and quartz powders. These two materials were similar as far as their fineness was concerned. They had (21) about the same geometrical surface area per gram; the calcium carbonate, however, had a smaller number of particles per gram (which is in the wrong direction as far as explaining our results is concerned). Making comparison of the dispersions in water, where solvation will be expected to be about the same, or of the dispersions in calcium chloride solution where both solvation and electrokinetic potential are about the same, it is observed from table 4 that the sedimentation volume is larger for the calcium carbonate than for the quartz. A greater attractive force is therefore indicated for calcium carbonate than for quartz. This conclusion is substantiated by the recent measurements of von Buzagh and Dux (7a) of the adhesion of particles to a plane surface of the same material. The angle of repose in the presence of water was 45° for calcium carbonate as against only 15° for quartz. According to the theory, κ should be smaller and *L.R.* larger for calcium carbonate than for

quartz when dispersed in the media mentioned. This is the result obtained, as seen from table 4.

(2) *Electrokinetic potential.* Of more importance generally than intrinsic attraction, which depends on the contribution of all atoms in a particle, is the attraction due to the nature and extent of surface of the particles of disperse phase. This attraction, it is important to note, can be readily varied.

Electrokinetic potential (originating at the surface) has an important bearing on the stability of colloidal suspensions, by virtue of its effect on the attraction between the micelles. The more closely the potential at the surface approaches zero, the greater is the force of attraction. von Buzagh (7) substantiated this by comparison of the adhesion and the potential of quartz particles in the presence of different electrolytes. At high electrolyte concentrations, however, other effects entered and modified the results.

Our measurements with a Mattson type cell showed that the calcium carbonate and quartz powders in table 4 were negatively charged. The cataphoretic velocity for calcium carbonate and quartz decreased to approximately zero in a 0.0025 and 0.050 *M* calcium chloride solution, respectively. The force of attraction between the particles is therefore greater in these solutions than in water. The sedimentation volume of quartz was correspondingly higher, but for some unexplained reason that of calcium carbonate appeared to be slightly lower. As was to be expected from the increase in potential to zero, κ decreased and *L.R.* increased when the dispersion medium was changed from water to the respective calcium chloride solutions (table 4).

(3) *Solvation.* The stability of lyophilic colloids is explained by the repulsion effect of a solvated film surrounding the surface of the micelles. Kruyt (16) has developed the theory in some detail. For the purpose of our problem it is important to observe that changing a dispersion from lyophilic to lyophobic increases the force of attraction between the particles, and *vice versa*. These changes were made in the following experiments, and the changes in plasticity and in cohesion observed.

Calcium carbonate and quartz are lyophilic in water and lyophobic in kerosene. The higher force of attraction between the particles in kerosene is shown by the large increase in sedimentation volume over that in water (table 4). At the same time, as expected, κ is much smaller and *L.R.* is much larger for the kerosene than for the water dispersion.

By dissolving sodium oleate in water the dispersion of calcium carbonate changes from lyophilic to lyophobic, owing to adsorption of oleate ion. Corresponding with this change in solution, sedimentation volume increases, and, as predicted by the theory, κ decreases while *L.R.* increases

(table 4). On the other hand, contrary results are obtained with quartz,—sedimentation volume decreasing, κ increasing slightly, and *L.R.* decreasing. This may be understood from the fact that quartz does not adsorb oleate ion.

By dissolving oleic acid in kerosene the dispersion of calcium carbonate in kerosene is changed from lyophobic to lyophilic, owing to adsorption of the acid. The resultant decrease in the force of attraction is shown in the very low sedimentation volume. Unfortunately the plastic flow constants of this dispersion could not be determined because of failure of the specimen, following discontinuous flow characterized by a single discontinuity. This mechanical failure, together with the characteristic wetness and excessive slump of the dispersion, were sufficient proof of its very low plasticity. The behavior of the dispersion of quartz in the same solution of oleic acid in kerosene was curious. No adsorption of oleic acid by the quartz would be expected, and the dispersion would therefore be expected to remain essentially lyophobic, as for quartz in kerosene alone. Actually a split behavior was shown. *L.R.* and sedimentation volume decreased, but κ also decreased,—from 2.4 to 1.3 (table 4). Corresponding to the lower value of κ , the dispersion of quartz in kerosene containing oleic acid was much easier to spread; in other words, it was clearly much more plastic than the dispersion in kerosene.

(4) *Dispersity*. By dispersity is meant the surface area per gram (or the number of particles per gram) of disperse phase as it exists in the dispersion. Obviously, the greater the dispersity, the greater the sum total force of attraction between the particles of disperse phase. The increase in plasticity on increase in fineness of the solid phase is so well known as not to require any further proof. It might simply be mentioned that the low plasticity for non-plastic kaolin ($\kappa = 2.4$, table 3) is due to its obvious coarseness relative to plastic kaolin. Similarly the regular increase in κ for mortars, with increase in the ratio of sand to cement (table 3), is a result of the regularly increasing coarseness of the more sanded mixtures.

A particularly instructive and important example of the effects of a change in dispersity is that furnished by light ball clay (English). The material labeled "unground" was granular and analyzed 14 per cent below the 200-mesh sieve and 7 per cent above the 28-mesh sieve. It is observed from table 4 that for the unground ball clay the plasticity depended definitely on the percentage of mixing water. When the per cent of water was decreased from 60 per cent to 46.7 per cent, κ decreased regularly from 1.08 to 0.91. The effect is explained by the greater work that could be performed on the paste during troweling, the stiffer it was. The increased work increased the dispersity by unlocking a larger number of primary particles from the secondary aggregates. Grinding this ball clay for 24 hr.

also helped in unlocking the primary particles, and, as a result, κ decreased very appreciably from 0.97 (average) to 0.82 (tables 3 and 4). *L.R.* at the same time increased from 52.5 per cent to 69.4 per cent, so that the ground clay was more cohesive than the unground product, as well as more plastic.

It was of great interest to study the effect of sodium hydroxide and hydrochloric acid solutions on the plasticity of the unground clay. The sedimentation volume was greater in solutions of 0.05 *N* sodium hydroxide and of 0.05 *N* hydrochloric acid than in water. As expected, κ was also less, while *L.R.* was greater (table 4). The increase in plasticity and cohesion is, however, appreciably greater with the alkali than with the acid.

The clay particles in water had a negative electrokinetic potential; 0.05 *N* sodium hydroxide, by decreasing the potential, would be expected to decrease the plasticity. On the other hand, the well-known dispersing effect of sodium hydroxide on clay would increase the plasticity. This dispersing effect apparently predominates over the reverse effect of decrease in the electrokinetic potential, and to it must be attributed the increase in plasticity.

The action of 0.05 *N* hydrochloric acid in increasing the electrokinetic potential would increase the plasticity. On the other hand, the dispersal or deflocculation of the clay is, if anything, diminished by the acid. The observed increase in plasticity may be attributed entirely to the increase in electrokinetic potential. Both the 0.05 *N* sodium hydroxide and 0.05 *N* hydrochloric acid increase the plasticity, but in a different way and to a different degree.

The comparative effect of 0.05 *N* sodium hydroxide and of grinding on the plasticity of the unground ball clay is observed from tables 3 and 4. The value of κ in the two cases is nearly the same. However, *L.R.* is much higher for the ground clay. Grinding therefore produced a more cohesive, though a no more plastic, product than that obtained by mixing the unground clay with 0.05 *N* sodium hydroxide.

(5) *Particle shape.* Shape of the particles of disperse phase probably affects the area of contact and the closeness of approach of the particles. Therefore an effect due to shape might be expected. Freundlich and Jones (10) find that suspensions of anisometric, especially plate-like, particles are thixotropic. If this is associated with an attraction (10), anisometric particles might be expected to give more plastic dispersions than regular particles, dispersity and other factors being equal.

DISCUSSION OF SPECIAL CASES

The behavior of shortening, a hydrogenated cottonseed oil, was unusual. It was apparent, as has been pointed out (13), that this material becomes "more plastic with mechanical working." Our observations for

(1) much mechanical working prior to test, (2) moderate working, and (3) very little working were as follows: κ , (1) 0.77, (2) 0.61, (3) 0.46, and p_0 , (1) 9.2, (2) 12.6, (3) 20.4. The increase in plasticity on mechanical working is therefore only apparent as it arises from a decrease in p_0 . The softness has been increased, but, because of the increase in κ , the plasticity actually has been lessened. The changes in p_0 and κ would accord with a possible coagulation of the particles of disperse phase on mechanical working.

The reason for the high plasticity of Portland cement paste (κ equal to 1.17, table 3), in spite of the comparative coarseness of the solid, is the presence of a film of freshly formed gel around each particle. The gel arises from hydrolytic decomposition of the cement. It may increase the total force of attraction, either by increase in the effective area of contact owing to unequal growth or deformation of the film, or by increase in specific attractive force due to unsaturated bonds at the surface.

With 29.0 per cent and 27.0 per cent of mixing water, the values of p_0 for the cement paste were 8.3 and 8.5, respectively, instead of the much higher values of 10.0 and 13.5 that would be expected from the results of table 3, applying equation 6. At the same time κ was 2.5 and 4.4, respectively, instead of the 1.17 obtained at the higher water contents. The unexpected increase in κ and disproportionate decrease in p_0 when decreasing the water content may be due to the onset of a repulsion between the cement particles when they are brought into too close conjunction. Such a repulsion would account also for the characteristic suspension of flow observed in the case of the cement pastes under the condition of high stress and corresponding close conjunction of the particles.

VISCOUS AND PLASTIC RESISTANCE

The effect of rate of deformation on dispersions is twofold. A change in rate may affect the plastic resistance or, more exactly, the constants of plastic flow. In the second place, a finite rate of deformation introduces an independent viscous resistance which is to be added to the plastic resistance to obtain the actual total resistance. At moderate rates of deformation the viscous component of resistance is usually comparatively small. Whatever its magnitude, however, the viscous component may be decreased to an indefinitely small value by decrease in rate of deformation, but the plastic resistance is inevitably present.

We shall not consider the question of viscous resistance *per se*, but primarily only the effect of rate of deformation on the magnitude of the constants of plastic flow. The effect of rate would be expected, in general, to be a second-order one, since plastic resistance depends by simple theory only on the static configuration of a plastic mass. Experiment shows that this expectation is justified.

When uniform loading of a plastic mass is stopped, the stress that was opposed to the viscous resistance is liberated and is free to produce an increment of plastic flow that adds itself to the plastic deformation at the instant loading was stopped. The situation is illustrated in figure 9, where it is seen that on cessation of loading at height h , a further flow at

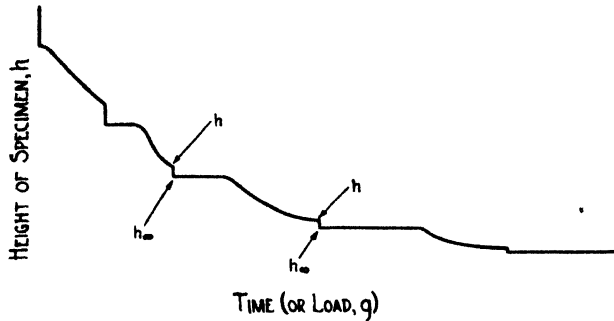


FIG. 9. Experimental curve when loading is stopped at intervals

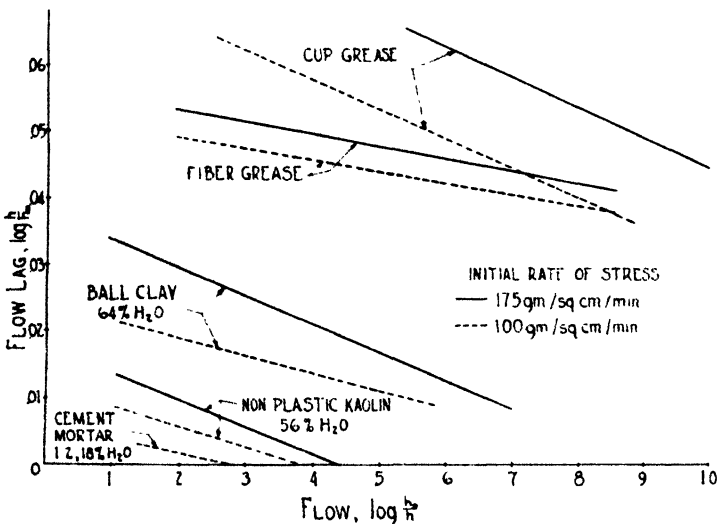


FIG. 10. Variation of plastic flow lag (due to viscous resistance) with plastic flow (referred to unit volume). Rate of loading is constant.

constant load takes place to height h_{∞} . The latter is the height that would correspond to the given load if this were applied "infinitely slowly." Hence, during finite rate of deformation there is a flow lag due to a viscous resistance which is proportional to $\log h/h_{\infty}$. The total flow at point h is proportional to $\log h_0/h$.

When loading is resumed after a period of rest, it is observed from

figure 9 that plastic flow does not immediately recommence, but an accumulation of stress, represented by the horizontal portion of the curve, first occurs.⁵ This is the stress that is necessary to overcome viscous resistance at the given rate of deformation. In our experiments the viscous resistance represented some 10 to 25 per cent of the total resistance at a rate of plastic flow during the first half-minute of 30 to 60 per cent per minute ($\log h_1/h_2$ per minute).

The effect of viscous resistance on the magnitude of the constants of plastic flow may be studied in a general way on the basis of the flow lag per unit volume. The latter has been plotted in figure 10 against total flow per unit volume. The relationship was roughly linear. The flow lag amounts to 5 to 10 per cent of the total flow, so that, owing to viscous resistance, the deformation is only 90 to 95 per cent of its maximum value at a given stress. The flow lag is smaller the smaller the rate of stress, as would be expected.

The results of figure 10 may be used to predict the general direction and the magnitude of the correction to κ and p_0 due to viscous resistance. The equation to the lines is

$$\log h/h_\infty = \log f_0 + s \log h_0/h \quad (8)$$

where s is the slope and $\log f_0$ is the intercept with the ordinate of zero plastic flow.

We now assume that equation 3 applies at "infinitely slow" rate of loading (where there is no viscous resistance). If we call $\bar{\kappa}$ and \bar{p}_0 the constants at "infinitely slow" rate of loading, substitute these into equation 3, and finally substitute into the resulting equation from equation 8, the following relation is obtained

$$(1 + s)\bar{\kappa} = \frac{\log p/f_0^2 \bar{p}_0}{\log h_0/h} \quad (9)$$

When equation 9 is compared with equation 3, the relation between the constants at finite rate of loading and at "infinitely slow" rate of loading is found to be

$$\bar{\kappa} = \kappa/1 + s \quad (10)$$

$$\bar{p}_0 = p_0/f_0^2 \quad (11)$$

By figure 10, s is negative and probably decreases with increase in rate of deformation, while f_0 is positive and increases with increase in rate. Therefore, the effect of finite rate of deformation is progressively to decrease the coefficient of renitence and to increase yield value.

⁵ The same result is obtained if the previously accrued load is first temporarily lifted, and then replaced.

A comparison of the constants for different materials at ordinary rates of loading with those at "infinitely slow" rate of loading is given in table 5. The values of $\bar{\kappa}$ and of \bar{p}_0 were obtained by plotting $\log h_\infty$ against $\log g$. For almost all dispersions it took but a minute or two to arrive at the required h_∞ from h . However, in the case of the very soft petrolatum and lanolin, the evidence was that it would take a much longer time. For these materials an interval of 1 hr. or 1.5 hr. was allowed for arriving at a value close to h_∞ . A special procedure was used and special care taken; the temperature during test varied by less than 0.5°C. Since the results were closely the same whether a 1-hr. or a 1.5-hr. interval was used, the

TABLE 5

Comparison of values of the plastic flow constants at "infinitely slow" rate of loading, $\bar{\kappa}$ and \bar{p}_0 , with the values at finite rate of loading, κ and p_0

DISPERSION	INITIAL RATE OF STRESS	$\frac{\bar{\kappa}}{\kappa}$	$\frac{\bar{p}_0}{p_0}$
	<i>grams per square centi- meter per minute</i>		
Lanolin, anhydrous	65	1.00	1.12(?)
Petrolatum	65	1.14	0.56
Cup grease	175	1.04	0.84
Cup grease	100	1.04	0.86
Shortening	175	1.02	0.87
Fiber grease	175	1.02	0.93
Fiber grease	100	1.02	0.94
Light ball clay	175	1.04	0.92
Light ball clay	100	1.03	0.95
Non-plastic kaolin	175	1.04	0.90
Non-plastic kaolin	100	1.04	0.93
1:2 cement mortar	100	1.04	0.92

values of table 5 represent the average of results obtained with the two different intervals of loading.

It is observed that, as anticipated, $\bar{\kappa} > \kappa$ and $\bar{p}_0 < p_0$ (with one exception). The difference is, however, small, considering the wide range of loading rate. $\bar{\kappa}$ never exceeded κ by more than 5 per cent, except for petrolatum for which the difference was about 15 per cent, while \bar{p}_0 was smaller than p_0 by less than 15 per cent, except again for petrolatum for which the difference was about 50 per cent. The ratios shifted slightly closer to unity when the rate of stress decreased from 175 to 100, about 0.2 per cent for $\bar{\kappa}/\kappa$, and 2 per cent for \bar{p}_0/p_0 .

To test further the question of rate of stress, numerous experiments were made on specimens varying in height and width by a factor up to 1.5, with rates of stress varying simultaneously between 20 and 175 g. per

square centimeter per minute (referred to the initial area). Height appeared to have a small systematic effect on the results, but, in general, differences in κ and p_0 were within the range of estimated error.

SUMMARY

Mixtures of solid and liquid, or dispersions, such as lanolin, grease, shortening, clay paste, lime putty, and cement mortar, although seemingly liquid, possess rigidity. The origin of the rigidity is structure of the disperse phase. As a result of their character as solids, dispersions interpose a static, or plastic, resistance to change of form, which increases with the extent of plastic deformation. The plastic resistance is inescapable, and is to be contrasted with viscous resistance, which depends on rate of deformation and may therefore be made indefinitely small. The sum of the plastic and viscous resistances make up in any actual case the total resistance that opposes change of form, but for moderate rates of stress the viscous resistance is usually relatively small.

Plasticity is a property related to plastic resistance. Its measurement on the basis of viscous resistance is deemed to be wrong in principle.

The present study of plasticity of dispersions is based on investigation of their plastic flow. A law of plastic flow has been found in which two constants are identified,—coefficient of renitence, κ , and yield value, p_0 .

Consistence, softness, and stiffness are terms relating to p_0 , while plasticity, and its converse, renitence, relate to κ . Workability is an ultimate property of concern to practice. It is compounded of softness (inverse of p_0) and plasticity (inverse of κ), both of which are required in sufficient degree to insure proper working of a dispersion.

A contrast between p_0 and κ consists in the fact that κ is generally of much greater moment in determining the stress at practical deformations. A more significant contrast, however, lies in the fact that p_0 varies with change of liquid content, while κ cannot be changed without changing the character of the system. Therefore κ is an essential constant; p_0 is an adventitious constant, but one whose particular magnitude is important and must be properly controlled.

Liquid retention, *L.R.*, is defined as the percentage of liquid phase at a specified yield value of reference. *L.R.* generally increases with increase in plasticity, in accord with practical experience. Its special significance consists in its being a measure of the cohesion or stickiness of a dispersion, subject, however, to the magnitude of κ .

A theoretical treatment is presented which is based on the premise that rigidity of a dispersion is due to the sum total force of attraction between the particles of disperse phase. Plasticity is determined by the sum total force of attraction at unit distance of separation of the particles. Factors that determine the total force of attraction, namely, intrinsic attractive

force, electrokinetic potential, solvation, and dispersity (also particle shape) are tested, and good agreement between the theoretically expected and the experimental results for plasticity and cohesion is obtained.

The effect of rate of deformation on the constants of plastic flow is studied, and is found usually to be small.

REFERENCES

- (1) BINGHAM, E. C.: Bull. Bur. Standards (No. 278) **13**, 309-53 (1916).
- (2) BINGHAM, E. C.: J. Rheol. **1**, 507-16 (1930).
- (3) BOGOMOLOVA, M. N., AND KUNIN, N. F.: J. Tech. Phys. (U. S. S. R.) **5**, 771-6 (1935).
- (4) BRADLEY, R. S.: Phil. Mag. **13**, 853-62 (1932).
- (5) BREWSTER, D.: Phil. Trans. Roy. Soc. **120**, 87-95 (1830).
- (6) BUZAGH, A. v.: Kolloid-Beihefte **32**, 114-42 (1930).
- (7) BUZAGH, A. v.: Kolloid-Z. **52**, 46-61 (1930); **51**, 105-12, 230-9 (1930).
- (7a) BUZAGH, A. v., AND DUX, K.: Kolloid-Z. **83**, 279-87 (1938).
- (8) CLEWS, F. H., MACEY, H. H., AND RIGBY, G. R.: Chemistry & Industry **57**, 221-7 (1938).
- (9) EHRENBERG: Bodenkolloid. Dresden (1918).
FREUNDLICH, H.: Kapillarchemie, Vol. II. Akademische Verlagsgesellschaft m.b.H., Leipzig (1932).
- (10) FREUNDLICH, H., AND JONES, A. D.: J. Phys. Chem. **40**, 1217-36 (1936).
- (11) GOODEVE, C. F., AND WHITFIELD, G. W.: Trans. Faraday Soc. **34**, 511-20 (1938).
- (12) HAMAKER, H. C.: Physica **4**, 1058-72 (1937).
- (13) HARVEY, A. W.: Ind. Eng. Chem. **29**, 1155-9 (1937).
- (14) HATSCHKE, E.: Kolloid-Z. **15**, 226-34 (1914).
- (15) KALLMAN, H., AND WILLSTAETTER, M.: Naturwissenschaften **51**, 952-3 (1932).
- (16) KRUYT, H. R.: Colloids (translated by van Klooster). J. Wiley and Sons, Inc., New York (1930).
- (17) McMILLEN, E. L.: J. Rheol. **3**, 179-95 (1932).
- (18) MELDAU, R., AND STACH, E.: J. Inst. Fuel **7**, 336-54 (1934).
- (19) NADAI, A.: Plasticity. McGraw-Hill Book Co., Inc., New York (1931).
- (20) NIEUWENBURG VAN, C. J.: First Report on Viscosity and Plasticity, Academy of Sciences of Amsterdam, pp. 141-72 (1935).
- (21) ROLLER, P. S.: J. Franklin Inst. **223**, 609-33 (1937); J. Am. Ceram. Soc. **20**, 167-74 (1937).
- (22) TOMLINSON, G. A.: Phil. Mag. **6**, 695-712 (1928).

THE CHROMATE-CHROMIC ELECTRODE POTENTIAL

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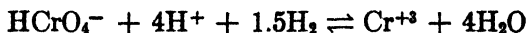
The value of 1.3 volts for the chromate-chromic electrode as reported by Luther (2) seems to be the only one given in the literature. A number of writers, in connection with other work, seem to question the interconvertibility of the chromate and chromic radicals (1). For these reasons we considered a further study desirable.

Since a solution of chromic perchlorate, according to Weinland and Ensgraber (3), retains its violet color and does not lose its high conductivity to the same degree as most chromic salts, we used perchloric acid and chromic perchlorate. The half-cell

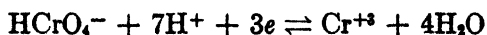


in which m represents the molalities, was studied at 25°C.

The data indicate that the cell reaction to represent the standard potential is



and for the half-cell is



If we assume that in dilute solutions the activities of the dissolved substances approach the molalities, and that that of water approaches unity, we have for the half-cell

$$E = E'_0 - \frac{0.0591}{3} \log \frac{m_{\text{Cr}(\text{ClO}_4)_3}}{m_{\text{H}^+}^7 \cdot m_{\text{HCrO}_4^-}}$$

and E'_0 approaches E_0 .

EXPERIMENTAL

When oxygen was present the irreversible potential of the oxygen electrode interfered, hence all of the work was done in the absence of air. The solutions were refluxed while nitrogen, freed from oxygen, was bubbled through. The bright platinum wire that served as the electrode was heated electrically to whiteness in a current of nitrogen. Except while

measuring, the whole set-up was under a slight excess pressure of purified nitrogen.

Conductivity water was used to recrystallize the substances and for the preparation of all solutions. A type K potentiometer and a Weston cell, both calibrated by the National Bureau of Standards, were used. A half-cell container with a coil of platinum wire, about 75 cm. of No. 26 gauge wire, contained the chromic-chromate solution. A heavier wire carried the current through the glass, thus permitting the heating of the smaller wire. In the first two series of measurements a hydrogen electrode with the same concentration of perchloric acid as that of the chromic-chromate electrode was used to give the same perchloric acid concentration through the whole cell. In the last series, as indicated, a saturated calomel electrode was used.

We measured three ratios of chromium trioxide-chromic perchlorate in molar perchloric acid against a hydrogen half-cell with the same concentration of perchloric acid. These cells initially gave widely divergent values but at different speeds approached the same value. Thus the most divergent speeds for the first electrode below were:

DAYS.....	0	1	3	5	6	8	11
	1.171	1.207	1.204	1.203	1.206		
	1.060	1.139	1.187	1.196	1.198	1.196	1.199

The last apparent equilibrium values were averaged for each half-cell measured, and the average of such values represents the voltage of the cell indicated. In no case did the maximum variations of values for any concentration exceed 30 millivolts.

$m\text{HClO}_4$	$m\text{CrO}_3$	$m\text{Cr}^{+3}$	E	ΔE
			volts	volts
1.000	0.001	0.100	1.203	0.039
	0.001	0.001	1.242	
	0.100	0.001	1.286	0.044

The calculated value for ΔE at constant acidity would be 0.0394 volt. The greater value, 0.044, is due to the effect of the 0.1 m CrO_3 increasing the actual acidity in the chromic-chromate electrode.

Continuing the preceding series for half-cells containing 0.001 molar chromium trioxide and 0.001 molar chromic perchlorate we varied the concentration of the perchloric acid. Using the mathematical equation given above

$$E'_0 = \Delta E_{\text{obsd.}} - \frac{0.0591}{2} \log (m_{\text{CrO}_3} + m_{\text{HClO}_4})^7 + 0.0591 \log m_{\text{HClO}_4}$$

$m_{\text{Cr}(\text{ClO}_4)_3}$	m_{CrO_3}	m_{HClO_4}	$\Delta E_{\text{obsd.}}$	E'_0
			<i>volts</i>	<i>volts</i>
0.001	0.001	1.	1.242	1.242
		0.5	1.215	1.239
		0.05	1.130	1.231
		0.01	1.037	1.188
		0.001	1.010	1.205

In the final series in which the saturated calomel electrode served as a reference, the molalities of the chromic perchlorate, chromium trioxide, and perchloric acid in the other half-cell were equal. Assuming that the molality of the acid is $2m$, from chromium trioxide and perchloric acid, we have

$$E'_0 = +0.2466 + \Delta E_{\text{obsd.}} - \frac{0.0591}{3} \log (2m)^7$$

m	ΔE	E'_0
	<i>volts</i>	<i>volts</i>
0.0333	+0.763	+1.171
0.0111	0.708	1.183
0.00333	0.643	1.190
0.00111	0.583	1.196
0.000333	0.509	1.194

The calculated values for the half-cell, using the more dilute solutions, indicate a value of 1.195 ± 0.010 volts for the standard chromic acid-chromate half-cell.

The calculated values we considered evidence that the half-cell was reversible. However, the slow change to constancy seems to indicate that the half-cell is near the "border line" of irreversibility. Likewise these calculated values confirm the originally assumed half-cell reaction.

SUMMARY

This study of the chromic-chromate-perchloric acid half-cell indicates a reversible oxidation potential of 1.195 ± 0.010 volts.

REFERENCES

- (1) GROSS AND HECKLING: J. Chem. Soc. **1937**, 325.
- (2) LUTHER: Z. physik. Chem. **30**, 652-6 (1899).
- (3) WEINLAND AND ENSGRABER: Z. anorg. Chem. **84**, 372 (1914).

INCREASING THE SOLUBILITY OF OILS IN WATER-SOAP SYSTEMS

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Until rather recently little attention has been given to Pickering's (4) observation that aqueous soap solutions can actually dissolve considerable proportions of certain oils. The emulsification of immiscible, or nearly immiscible, liquids with the aid of soaps diverted attention from this important observation. Smith (5) greatly extended Pickering's experiments and announced that "every organic liquid that has been investigated is many times more soluble in soap solution (e.g., 10 per cent sodium oleate) than in water." Hartley (1) and Lawrence (3) have discussed the mechanism of this solvent process. They also called attention to the improvements claimed in the detergent value of soaps owing to the presence of certain dissolved oils. Lysol, so Hartley noted, is a solution, not an emulsion, in soap and water. Smith reminded investigators of vitamins A and D that the sterols, hydrocarbons, etc., released from fish oils by saponification have considerable solubility in the soaps formed and considerable resistance to solvent extraction. He considered ether, in the presence of alcohol, to be the best extractive.

It occurred to the author, after reading the Kramer (2) patent on the preparation of a detergent paste, that the influence of pine oil on the solubility of such paraffin hydrocarbons as common kerosene merited some study. This seemed to be an extension of the work referred to above, for in this case a fourth substance of polar-non-polar nature was added. Pine oil distilled from old stumps is known to be an oxidized product with polar hydroxyl groups in the molecule. It is not merely pinene, a hydrocarbon.

EXPERIMENTAL

No special efforts were made to secure unusually pure materials. A good grade of sodium oleate was rubbed well at room temperature with the desired amount of water, using a flexible spatula. The *mixing* was carried on intermittently for about 30 min., the minimum time found effective as preparation for the rest of the experiment. After allowing the soap paste to stand for another 30-min. period, the mixture of kerosene

TABLE 1
Solutions of soap-water-pine oil-kerosene

PROPORTIONS BY WEIGHT				APPEARANCE AND STABILITY
Sodium oleate	Water	Pine oil	Kerosene	
1	4	4	4	Clear as water. Stable after 3 months
1	2	2	2	Clear as water. Stable after 3 months
1	2	4	4	Opalescent. Almost transparent
1	6	4	4	Almost as clear as water. Slight precipitation after 2 months
1	8	1	2	Almost as clear as water. Opalescent
1	8	4	4	Opalescent. Almost transparent. Slight precipitation after 3 months
1	8	2	2	Opalescent. Precipitate settled in 4 weeks
1	8	5.5	4	Opalescent. Much precipitation in 2 months
1	8	8	4	Opalescent. Nearly clear. Two layers on standing
1	8	4	1	Opalescent. Two layers after 3 months
1	8	2	4	Faintly opalescent. Two layers in 2 months
1	8	4	2	Two layers: upper opalescent, lower clear
1	8	12	3	Two layers in 3 months: opalescent upper layer, clear lower layer
1	8	12	4	Very opalescent. Stable after 3 months
1	8	12	6	Two layers: upper opalescent, lower clear with precipitation
1	8	2	8	Fluid, creamy-white emulsion

TABLE 2
Solutions of soap-water-pine oil-benzene

PROPORTIONS BY WEIGHT				APPEARANCE AND STABILITY
Sodium oleate	Water	Pine oil	Benzene	
1	8	4	4	Opalescent. In 2 months small lower layer separated
1	8	8	4	Quick separation into 2 layers and precipitation
1	8	1	1	Opalescent. Two layers and precipitation after few weeks
1	8	8	2	Faintly opalescent. Stable after 2 months
1	4	8	2	Two clear layers with precipitation between after standing 2 months

and pine oil was then beaten into this soap paste with a high-speed mixer, using such volumes and such a vessel that air was not whipped in.

The various liquid products obtained by varying the proportions of water, sodium oleate, kerosene, and pine oil were compared as to transparency, formation of two layers, formation of precipitates, and stability during the two or three months following. The results are shown in tables 1 and 2.

A mixture of 1 part (by weight) of sodium oleate, 8 parts of water, 8 parts of pine oil, and 4 parts of carbon tetrachloride looked like a milky emulsion and quickly separated into layers and a precipitate. Evidently carbon tetrachloride is unusually difficult to dissolve in this system. Even benzene is somewhat more difficult in this respect than the paraffin hydrocarbons.

Clove oil, containing engenol, which somewhat resembles pine oil in its phenolic nature, is inferior to pine oil in aiding the solution of hydrocarbons, yet it has some effect.

DISCUSSION

Other workers have offered theories of the action of sodium oleate or other soaps in aiding the solution of hydrocarbons in water. It has been suggested that the colloidal soap micelles dissolve the oil and also that polar and non-polar binding of the components accounts for the phenomenon.

It seems to the author that the pine oil as a new component aids chiefly by the use of its hydroxyl groups in polar attraction for the water and for the polar group of the soap. Of course its large non-polar radical also attracts the hydrocarbon and the non-polar radical of the soap. In other words, pine oil molecules act as binding links for the soap-water-hydrocarbon.

Table 1 shows the limiting proportions. The best products by far are those represented by 1, 4, 4, 4 or 1, 2, 2, 2 parts by weight of sodium oleate, water, pine oil, and kerosene. In these the weights of the three liquids are equal. Other interesting products of different proportions are more or less opalescent and yet rather transparent. These are less stable and, when aged, exhibit a silky, almost curdy, flow. Evidently curd fibers of solvated soap are present. It is significant that the 1, 4, 4, 4 and 1, 2, 2, 2 solutions do not show this silky flow on tilting the bottles.

Since pine oil is a well-known detergent, some of these combinations may have exceptional value as detergents or as cutting oils.

SUMMARY

It is shown that pine oil in proper proportions greatly increases the known solubility of paraffin oils in water containing sufficient sodium oleate. Optimum proportions for producing perfectly transparent, stable solutions are 1, 4, 4, 4 and 1, 2, 2, 2 parts by weight of sodium oleate, water,

pine oil (the oxidized type), and kerosene. This means that a given weight of water (containing sodium oleate) can dissolve twice its own weight of the two oils.

With benzene as hydrocarbon the optimum proportions are 1, 8, 8, 2 parts by weight.

REFERENCES

- (1) HARTLEY, G. S.: Wetting and Detergency, p. 153. The Chemical Publishing Co., New York (1937).
- (2) KRAMER: U. S. patent 1,927,872.
- (3) LAWRENCE, A. S. C.: Wetting and Detergency, p. 203. The Chemical Publishing Co., New York (1937).
- (4) PICKERING, S. U.: J. Chem. Soc. **111**, 86 (1917).
- (5) SMITH, E. LESTER: J. Phys. Chem. **36**, 1401, 1672, 2455 (1932).

THE ELECTRICAL CONDUCTANCE OF SOLS AND GELS AND ITS BEARING ON THE PROBLEM OF GEL STRUCTURE. I

GELATIN

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The problem of gel structure is one of great complexity, and there exists a considerable divergence of opinion among colloid chemists as to the interpretation of the heterogeneous data in this field. All of the theories that have been proposed may be divided into the following classes:

The one-phase, or solid solution, theory is supported by Proctor (20) and by Katz and Robinson (16), who hold that a gel is a solid solution of the dispersion medium in a second constituent, both constituents being within the range of molecular attractions of each other. This theory fails to explain many of the properties of gels, especially the loss of mobility on setting.

The two-phase, liquid-liquid theory, in which gels are assumed to be similar in structure to emulsions, is supported by Quincke, Hardy, Wo. Ostwald, and Garrett. This concept has difficulty in explaining the fact that no emulsion has ever been converted into a jelly, and Hatschek (13) argues that the theory is untenable because it is physically impossible from purely geometrical considerations to account for the elasticity shown by gels.

The two-phase, solid-liquid theory was first suggested by Frankenheim in 1835, who considered gels to be composed of aggregates of small crystals with pores between them. In 1879 von Nägeli proposed that gels were composed of molecular complexes or micelles with crystalline properties, separated by skins of water and forming meshes or interstices in which the water is contained by molecular attraction. Bachman (2) studied the process of gelation microscopically, and found that, as the sol began to set, there were formed small elements consisting of submicrons and, in part, microns, which gradually lost their translatory motion. Finally the

whole field was filled with cohering particles without any motion. Kruyt (17) concludes that this is the most satisfactory representation of gelation. Bachman and Zsigmondy (3) later observed a fibrillar structure in addition to the grainy structure, which is quite sharply defined in the case of soap jellies. Laing and McBain (18) consider the gelation of soap to result from the linking up of colloidal particles to form a filamentous structure.

From his work on foams Bütschli was led to the opinion that many gels have a fine honeycomb structure which could be made visible with a hardening agent. Pauli and others have raised objections to this theory, on the ground that the honeycomb structure may have been caused by the treatment by the hardening agent. Copisarow (7) has produced such a structure by diffusing tanning agents into a gelatin gel.

Bradford (5) has proposed the theory that the reversible sol-gel transformation is an extreme case of crystallization. He is supported in his views by the researches of von Weimarn, who has prepared gels of the sulfates of calcium, barium, and strontium by precipitation from solutions of proper concentration. He states that there is no fundamental difference between these gels and ordinary jellies such as agar and gelatin. Weiser does not agree that all gels are crystalline, and cites evidence by Scherrer (21) and Harrison (12) to show that the spherites of gelatin and starch are not crystalline in character.

This brief summary of the more outstanding theories of gel structure illustrates the great variance of opinion and the many difficulties involved in the interpretation of the complex phenomenon involved in gelation. In the study of gel structure the measurement of many properties has been undertaken, namely, diffusion, viscosity (plasticity), optical properties, ultramicroscopic behavior, tensile strength, elasticity, compressibility, setting point, etc., but little attention has been paid to the electrical conductance of gels. Apart from the work by McBain on soap jellies, no extensive investigation has been made in this field.¹ The work herein reported was undertaken in order to obtain such data for a number of gel systems and to apply the results as evidence for one or more of the above theories. While it is hoped that the study can be extended to other gel-forming materials, this report is concerned only with gelatin-water or gelatin-salt-water systems.

EXPERIMENTAL PROCEDURE

The Wheatstone bridge method was used in determining conductivity, using a Leeds and Northrup slide wire of Kohlrausch design. An audion tube was the source of the oscillating current. The refinements recom-

¹ In addition to the work of McBain, mention should be made of the brief report of Hurd and Swanker (*J. Am. Chem. Soc.* **55**, 2607 (1933)), who state that the conductances of silica sols and gels are practically the same.

mended by Jones and Josephs (15), and used by Edson and Rexroth (10) in a study of the conductance of electrolytes, were employed. The capacity of the conducting cell was balanced in parallel by an adjustable condenser. Two conductivity cells of the ordinary plunge type were used, one with a cell constant of about 0.4 and the other of approximately 0.1, the latter cell being used for the pure gelatin gels and the very dilute electrolyte solutions. The electrodes in the cells were rigidly braced, and the cell constant of each cell was determined after each trial to make sure that any changes in conductance were not due to changes in the positions of the electrodes. Measurements were made on the potassium chloride solution used for determinations of the cell constant over a period of four days to determine whether any error due to absorption might occur. No change was noted. Tests of the sensitivity of the method used both on the calibrating solution and on the actual conductivity measurements showed the method to be accurate to at least 0.1 per cent.

All salts used were of c. p. grade and were further purified by recrystallization. After purification they were dried carefully to constant weight. Eastman ash-free gelatin was employed in all cases. Moisture determinations on this material gave an average value of 15.16 per cent. Determinations of the ash content showed that the maximum value did not exceed 0.02 per cent on any samples used. The sols of gelatin were made up according to the following standard procedure, in order to minimize any complicating effects that are dependent upon the history of gelatin sols: Gelatin was weighed out carefully and the approximate amount of conductivity water needed was added. The system was then kept at 45°C. for 1 hr. The gelatin became swollen and with occasional agitation was completely dispersed in another hour. The flask was then cooled and weighed to obtain the amount of water present.

The conductivity measurements were made at 25° and at 30°C., the maximum variation in temperature being 0.01°C. The conductance of the specimen in the sol state was first determined. It was then allowed to set slowly overnight at room temperature (20–25°C.). The conductance of the gel was determined the following morning. It was found that sols which were set more rapidly by immersing them in an ice bath would melt more rapidly and at a lower temperature. When the sols were set slowly it was comparatively easy to get readings on the gel state of even some of the most dilute gels at 30°C. These data agree with the facts reported by Olson (19) in his study of the change of setting time with the temperature at which the sol was set. Olson assumes that at a higher temperature the building up of chains of molecules during the setting process is more complete. According to him, a gel setting rapidly is composed of short chains only slightly interlaced and is thus more easily redispersed.

THE ELECTRICAL CONDUCTANCE OF PURE GELATIN SOLS AND GELS

The results obtained from conductance measurements on the system gelatin-water are summarized in table 1 and shown graphically in figure 1. The specific conductance of the sol is consistently greater than that of the gel in the range of concentrations used. The difference between sol and gel increases with increasing concentration, and the increase is more rapid at 30°C. than at 25°C. This is clearly shown in figure 1 by the spreading of the curves with increasing concentration.

The change of conductivity with temperature is greater for the sol state, the temperature coefficient being on the average about 25 per cent more.

TABLE 1
Specific conductance of the system gelatin-water

GELATIN*	TEMPERATURE	pH	SPECIFIC CONDUCTANCE		DIFFERENCE SOL - GEL
			Gel	Sol	
per cent	°C.		mhos	mhos	
4.58	30	4.80	5.96×10^{-5}	6.20×10^{-5}	0.24×10^{-5}
4.58	25		5.89×10^{-5}	6.13×10^{-5}	0.24×10^{-5}
4.63	30	4.81	6.10×10^{-5}	6.39×10^{-5}	0.29×10^{-5}
4.63	25		5.95×10^{-5}	6.20×10^{-5}	0.25×10^{-5}
5.99	30	4.85	7.90×10^{-5}	8.46×10^{-5}	0.56×10^{-5}
5.99	25		7.17×10^{-5}	7.53×10^{-5}	0.36×10^{-5}
6.41	30	4.88	8.49×10^{-5}	9.09×10^{-5}	0.60×10^{-5}
8.31	30	4.90	10.46×10^{-5}	11.26×10^{-5}	0.80×10^{-5}
8.31	25		9.27×10^{-5}	9.71×10^{-5}	0.44×10^{-5}
13.2	30		12.44×10^{-5}	13.35×10^{-5}	0.91×10^{-5}
13.2	25		11.68×10^{-5}	12.35×10^{-5}	0.67×10^{-5}

* Per cent gelatin = $\frac{\text{grams of dry gelatin (corrected for moisture content)}}{\text{grams of water}} \times 100$.

The pH value (determined by the use of the quinhydrone electrode) of the most dilute sol was 4.80. Slight increases in pH were observed at higher gelatin concentrations. A pH of 4.8 corresponds to a hydrogen-ion concentration of approximately 2×10^{-5} gram-moles per liter, a value which could not account for more than 0.7×10^{-5} mhos of the specific conductance of the sols. The ash, less than 0.02 per cent in amount, might also account for a part of the conductance. The Eastman Kodak Company informs us, however, that actual analyses of the ash content of their "ashless" gelatin, which was employed in our study in all cases, consists almost entirely of silica. The form of the silica as present in our sols and gels is unknown but in any case, whether present as free silicic acid, colloidal silica, or in some other form, its actual conductance is probably small. This conclusion may best be realized when compared with the

calculated conductance of a strong electrolyte. If, for example, the ash was entirely calcium oxide, present to the amount of 0.02 per cent, the calcium ion, if we assume complete dissociation from the gelatin, would have a specific conductance of 2×10^{-5} mhos, that is, about one-third of the total specific conductance. It is thus evident that both in the sol state and in the gel state, gelatin itself is the major conductor of the current. Further, the decrease in conductance from sol to gel state, in the cases studied, lies only between 4 and 8 per cent.

If gelatin micellae are therefore the chief conductors in both sol and gel state, it is evident that gelation does not seriously obstruct the conduction process. Without doubt the gelation process has decreased very considerably, if not destroyed, the mobility of the gelatin micellae. The small

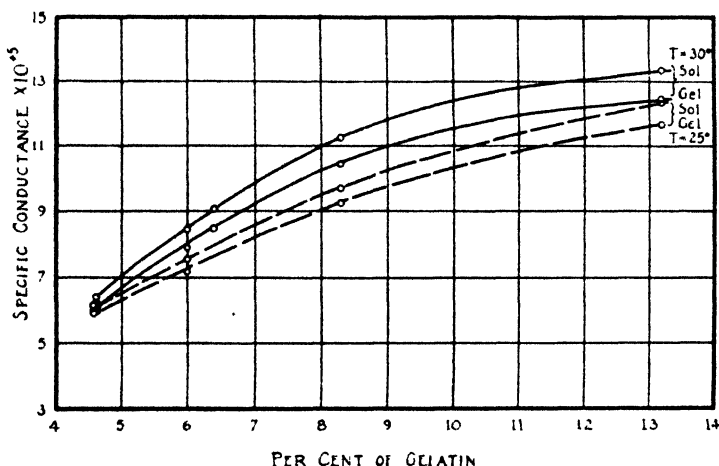


FIG. 1. Conductance measurements on the system gelatin-water

decrease in conductance upon gelation appears, therefore, at first thought, to be difficultly explainable. The two factors become reconcilable if it is assumed that *the liquid phase exists as the continuous phase in both sol and gel states.*

Conduction in the sol state is then largely cataphoresis; upon gelation the process has changed from cataphoresis to electroendosmosis. In the sol state the gelatin micellae move in the liquid phase; in the gel state the liquid moves past the fixed gelatin micellae, each of which may possess surface conduction. Upon the basis of such an explanation, the small decrease in conduction upon gelation would be due to the decreased surface of contact of gelatin micellae with the liquid phase, and to the somewhat greater length of path that any ion current carriers must of necessity traverse when gelation takes place. It will be understood that such an explanation assumes also the necessity of a continuous phase of the gelatin micellae in

the gel state in order to account for the rigidity of the gel. The conductance of gelatin sol and gel is thus in accord with the fibrillar theory of gel structure.

TABLE 2
Specific conductance during sol-gel transformation

AGE	SPECIFIC CONDUCTANCE	REMARKS
Gelatin sol at 25°C.; 5.99 per cent gelatin		
hours	mhos	
0	0.0000753 ₄	Sol
0.5	0.0000745 ₁	Setting in parts; soft meniscus
1	0.0000736 ₈	Soft jelly; part liquid
14	0.0000716 ₉	Gel set solid overnight
16	0.0000716 ₉	Gel; no change
Gelatin gel at 30°C.; 6.41 per cent gelatin		
0	0.0000848 ₇	Gel (set rapidly at low temperature)
3.5	0.0000860	Meniscus soft
5	0.0000865	Soft jelly; viscous
6	0.0000871	Viscous sol; about melted
9	0.0000908 ₈	Sol state
9.25	0.0000908 ₈	Sol; no change

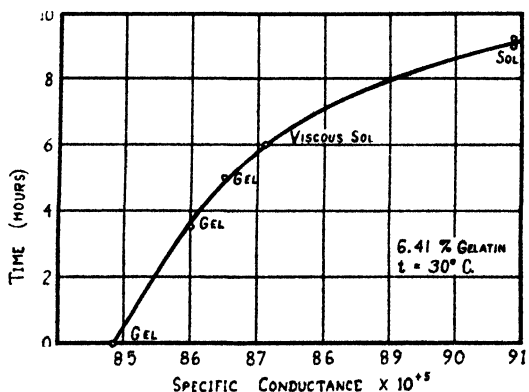


FIG. 2. Conductance measurements taken as gelation and redispersion were in progress

In the case of the 5.99 per cent and 6.41 per cent sols, conductivity measurements were taken as gelation and redispersion processes were in progress. The data given in table 2 (see also figure 2) show that the gelation and redispersion processes are gradual and continuous, and the ease with which the change is accomplished is evidence for the theory that the two phases

present in the sol and gel state are not extremely different in their composition.

Yabuki (24), who was interested primarily in the effect of added salts on the conductivity, includes also some data on the conductance of pure gelatin gels. His values are approximately ten times those reported here, but since he makes no specifications concerning the ash content this difference may be easily accounted for by a high ash content. Greenberg and Mackey (11) have reported on the conductivity of pure gelatin sols and gels within the range of concentrations of 0.9 and 4.58 per cent. The highest percentage reported is the only result comparable to those reported here; the conductance is of the same magnitude but slightly higher. In general their results as to the difference in conductance between sol and gel are in good agreement with those of table 1.

It should also be pointed out that the difference in conductivity between sol and gel state cannot be accounted for upon any difference in the specific volume of the two phases. As we have pointed out elsewhere (22), there is a slight contraction in volume when the sol solidifies. This contraction, for gelatin concentrations up to 10 per cent at least, is less than 0.01 per cent of the volume of the sol. Furthermore, such a change in volume should produce an increase (rather than the observed decrease) in specific conductance of the gel state over the sol state, as the number of current carriers per unit of volume would be greater in the gel state than in the sol state provided no other changes occurred.

ELECTRICAL CONDUCTIVITY OF ELECTROLYTES IN GELATIN SOLS AND GELS

The first studies in this field were made by Arrhenius (17) in 1885 when he determined the conductivity of sodium chloride, zinc sulfate, and copper acetate in a gelatin solution which set to a gel at 24°C. He allowed a 4.2 per cent sol to cool slowly and found no discontinuity in the temperature-conductivity curve at the setting point and no appreciable difference in conductivity of the sol and gel state. In 1889 Indeking (18) measured the viscosity and conductivity of zinc sulfate solutions containing up to 50 per cent gelatin. He found no discontinuity in the temperature-conductivity curve at the setting point. Dumanski (9) studied the conductance of salts in gelatin sols only and made no measurements on the gel state. Further consideration of his results is given below.

McBain and Laing (18) investigated the conductance of soap solutions. Their results indicate that there is no difference in the conductance of sodium oleate in the sol and the gel state. These authors assume that the colloidal soap arises from, and is in true equilibrium with, the crystalloidal constituents. Yabuki (24) compared the conductance of potassium chloride in water and in gelatin and again in the gel state. His results will be considered later, together with those of Greenberg and Mackey (16),

TABLE 3

*The electrical conductance of salts in gelatin sols and gels**

GEL CONCENTRATION	CONCENTRATION OF KCl	TEMPERATURE	SPECIFIC CONDUCTANCE $\times 10^3$			A		$Y \times 10^3$		$(k - y) \times 10^3$	$\frac{k - y}{C} \times 10^3$
			Sol	Gel	Difference	Sol	Gel	Sol	Gel	Sol	
per cent	N	°C.									
4.53	0.00101	25	13.48	13.31	0.17	134.2	133.1	7.18	7.23	7.52	1.7
4.53	0.00505	25	65.30	64.90	0.40	130.6	129.8	59.0	58.8	12.7	2.8
4.53	0.0101	25	126.7	126.5	0.20	126.7	126.5	120.4	120.4	20.3	4.4
4.53	0.0505	25	579.5	579.0	0.00	115.9	115.8	573.2	573.0	92.0	20.0
4.58	0.1008	25	111.2	111.2	0.00	111.2	111.2	110.2	110.0	187.0	40.0
4.58	0.1006	30	123.2	123.2	0.00	123.2	123.2	122.6	122.6	183.0	40.0
4.58	0.2508	25	263.5	263.5	0.00	105.4	105.4	262.4	262.4	450.0	98.0
4.58	0.499	25	499.9	499.9	0.00	99.98	99.98	499.3	499.3	870.0	191.0
4.63	0.0101	25	124.7	124.5	0.2	124.7	124.5	128.5	128.6	12.1	2.6
4.63	0.0101	30	138.3	137.7	0.6	138.3	137.7	131.9	131.6	23.0	4.9
4.63	0.1008	25	110.7	110.7	0.00	110.7	110.7	110.1	110.1	181.0	40.0
4.63	0.1007	30	120.1	120.1	0.00	120.1	120.1	119.5	119.5	214.0	46.0
4.63	0.499	25	499.0	499.0	0.00	98.8	98.8	498.4	498.4	876.0	190.0
4.63	0.498	30	526.5	526.5	0.00	105.3	105.3	525.9	525.9		
8.31	0.00511	25	59.07	58.62	0.45	118.15	117.25	49.36	49.0	32.5	3.9
8.31	0.00510	30	65.15	64.60	0.56	130.3	124.2	53.89	54.2		
1.31	0.01022	25	114.8	114.7	0.1	114.8	114.7	105.1	105.4	35.6	4.3
8.31	0.01021	30	127.15	127.5	0.35	127.15	127.5	116.0	117.0	38.6	4.6
8.31	0.1018	25	102.0	102.0	0.00	102.0	102.0	1017.0	1017.0	271.	32.5
8.31	0.1017	30	111.7	111.7	0.00	111.7	111.7	1106.	1107.	303.	40.9
8.31	0.5037	25	445.1	445.1	0.00	89.03	89.03	444.2	444.2	1420.	170.
8.31	0.5028	30	488.9	488.9	0.00	97.78	97.78	387.8	487.8		
	CONCENTRATION OF KSCN										
	N										
3.2	0.1	27	956.5	955.1	0.6	95.6	95.5	944.0	943.	417.	32.
5.99	0.01015	25	108.6	108.6	0.00	108.6	108.6	101.1	101.4	33.3	5.5
5.99	0.1009	25	973.0	973.0	0.00	97.3	97.3	967.	967.	231.	39.
5.99	0.2008	25	1847.	1847.	0.00	92.29	92.29	1840.	1840.	440.	73.

*A = equivalent conductance.

Y = (specific conductance of salt in gelatin) - (specific conductance of gelatin).

 $k - y$ = (specific conductance of aqueous salt solution) - Y; or decrease due to presence of gelatin. $\frac{k - y}{C}$ = decrease per gram of gelatin in 100 g. of sol.

who determined the conductivity of hydrogen chloride, sodium hydroxide, and sodium chloride in sols and gels of gelatin.

With this background of comparative data, the following determinations

have been made: First, the conductance of the purified salts was determined and compared with the values given by the International Critical Tables and by Kohlrausch and Holborn. The agreement was satisfactory (within 0.1 per cent) and checked the purity of the salts and the experimental method used.

Table 3 gives the results obtained for potassium chloride of concentrations from 0.001 *N* to 0.5 *N* in several gelatin sols and gels. These results for 25°C. are shown graphically in figure 3. The equivalent conductance curves of potassium chloride in gelatin sols and gels follow those of potassium chloride in aqueous solutions in general, and have about the same slopes. The presence of gelatin causes a decrease in conductance, however,

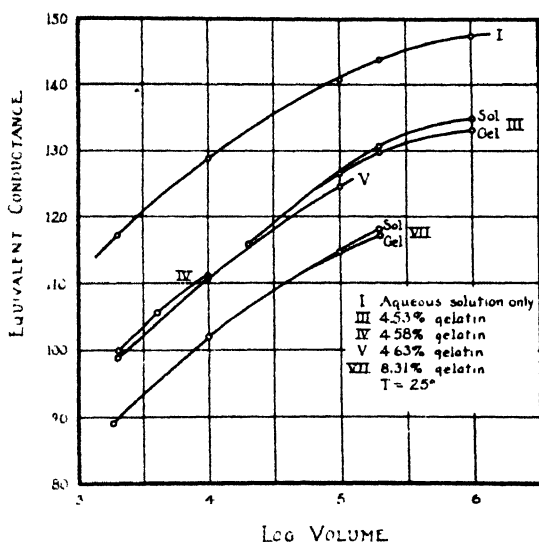


FIG. 3. Equivalent conductance of potassium chloride in gelatin sols and gels

and this decrease is greater as the gelatin content increases. The conductivity was also the same in the gel as in the sol state down to salt concentrations of 0.01 *N* to 0.001 *N*. Here the equivalent conductance was slightly greater in the sol than in the gel state. However, at this low salt concentration the conductance of the gelatin itself becomes an appreciable factor. If the specific conductance of pure gelatin is subtracted from the total specific conductance, these differences between the sol and the gel state are practically removed. It will be recalled that the conductance of pure gelatin in the sol state was greater than in the gel state, and this difference accounts for the spreading of the sol-gel curves at low salt concentrations.

The fact that the conductance of potassium chloride in gelatin sol and

gel is the same is interpreted by us as meaning that the ions move with equal freedom in both cases. The only difference is that in the sol state the gelatin particles move also, while in the gel state their movement is more restricted. Evidently in the sol state there are large interstices between the gelatin particles which permit the movement of ions, and during the setting process these particles orient themselves in such a way that a rigid system is produced, but the interstices are not thereby reduced to a great extent. These data, we believe, are again evidence for the "brush-heap" or fibrillar theory of gel structure, in which both phases are considered continuous.

The temperature coefficient of the specific conductance of potassium chloride in gelatin (both sol and gel are the same) over the limited range of 25°C. to 30°C. is given in table 4.

The temperature coefficients of conductance for gelatin sols are of the same order of magnitude as those for aqueous solutions. This is in agree-

TABLE 4
Temperature coefficient of specific conductance

CONCENTRATION OF GELATIN	0.01 N KCl	0.1 N KCl	0.5 N KCl
<i>per cent</i>			
4.58		0.000240	
4.63	0.0000270	0.000190	0.00055
8.31	0.0000247	0.000194	0.00087
0.00	0.0000278	0.000242	

ment with the work of Arrhenius (1) on salts in gelatin. Indeking (14) found that the temperature coefficient was no longer independent of concentration at high gelatin concentrations (50 per cent). There is a slight tendency, as shown in the data presented in table 4, for the temperature coefficient to decrease with increasing gelatin concentration. Since the loss of fluidity due to gelation has been shown not to affect the conductivity, the change in viscosity at 25°C. and 30°C. could not account for this. However, if ion adsorption on gelatin micellae occurs, it is possible that these ions are not freely liberated at higher temperatures; consequently, as the gelatin concentration increases, the temperature coefficient becomes lower.

Further information which may be interpreted as bearing upon ion adsorption was obtained by using solutions of potassium thiocyanate in gelatin, and comparing the decrease in conductivity in gelatin with the decrease in potassium chloride sols and gels. The last three values of table 3 were a preliminary attempt to investigate this point, where it was found that $(k - \gamma)/C$ (the decrease in specific conductance per unit concentration of gelatin) showed that a greater decrease occurred in the thio-

cyanate solutions containing 5.99 per cent gelatin than for potassium chloride solutions containing 8.31 per cent gelatin. This suggested a more

TABLE 5

The specific conductance of aqueous potassium chloride and potassium thiocyanate solutions at 45°C.

SALT CONCENTRATION	SPECIFIC CONDUCTANCE = k <i>mhos</i> $\times 10^4$	Λ	DENSITY	$\eta_e/\eta_{H_2O}^*$	η_e^\dagger
Water.....			0.99022	1.0000	0.00597
0.00495 N KCl.....	99.30	198.6	0.99025	0.9982	0.00596
0.00989 N KCl.....	196.3	196.3	0.9905	0.9930	0.00593
0.04944 N KCl.....	917.5	183.5	0.9924	0.9993	0.005955
0.09875 N KCl.....	1742.	174.2	0.9948	1.0027	0.00599
0.00495 N KSCN.....	91.35	182.7	0.9900	1.0012	0.00598
0.00988 N KSCN.....	180.5	180.5	0.9897	1.0005	0.00597
0.04932 N KSCN.....	849.5	169.9	0.9906	1.0034	0.00599
0.09835 N KSCN.....	1627.	162.7	0.9936	1.0070	0.00603

* Relative viscosity.

† Absolute viscosity.

TABLE 6

*The specific conductance of potassium chloride and potassium thiocyanate in 4.5 per cent gelatin at 45°C.**

SALT CONCENTRATION	SPECIFIC CONDUCTANCE <i>mhos</i> $\times 10^4$	Λ	Y <i>mhos</i> $\times 10^5$	Λ_c	$k - y$ $\times 10^4$	DENSITY	η_e/η_{H_2O}	η_e
4.5 per cent gelatin....	9.02					1.0040	4.600	0.02745
0.00502 N KCl.....	92.12	184.2	83.1	166.2	16.2	1.0040	4.634	0.02778
0.01003 N KCl.....	177.6	177.6	168.6	168.6	27.7	1.0040	4.754	0.02838
0.05015 N KCl.....	811.5	162.3	802.5	160.5	115.0	1.0067	4.874	0.02910
0.1000 N KCl.....	1559.	155.9	1550.	155.0	192.0	1.0075	5.007	0.02991
0.00502 N KSCN.....	83.22	166.4	74.2	148.4	17.1	1.0040	4.628	0.02763
0.01003 N KSCN.....	160.5	160.5	151.5	151.5	29.0	1.0040	4.621	0.02759
0.05006 N KSCN.....	737.0	147.4	728.0	145.6	121.5	1.0060	4.741	0.02831
0.998 N KSCN.....	1437.	143.7	1428.	142.8	199.0	1.0080	4.891	0.02920

* Λ = equivalent conductance.

Y = (specific conductance of salt in gelatin) - (specific conductance of pure gelatin).

Λ_c = equivalent conductance calculated from Y .

$k - y$ = (specific conductance of salt in water) - Y ; or decrease due to presence of gelatin.

η_e = absolute viscosity of electrolyte-gelatin system.

extended study of thiocyanate and chloride solutions at a lower concentration and at a temperature well above the setting point of such systems.

Table 5 gives the data on aqueous solutions at 45°C. Table 6 (see also figure 4) gives data on 4.5 per cent gelatin-salt solutions and includes viscosity and density data as well as conductivity readings.

The Hofmeister series is common to a variety of phenomena in colloidal chemistry, crystalloidal chemistry, and biology. The thiocyanate ion occurs at that end of the Hofmeister series where the ions have the ability to peptize negatively charged emulsoids, decrease the time of gelation, enhance swelling, etc. The chloride ion is located somewhat nearer the other end of the series. Column $k - y$ of table 6 shows the decrease in conductivity of potassium chloride and potassium thiocyanate due to the presence of 4.5 per cent gelatin. The decrease is approximately 5 per cent

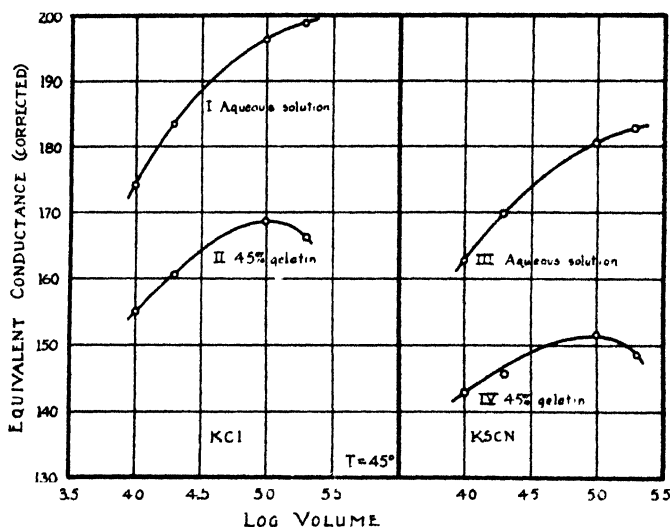


FIG. 4. Equivalent conductance of 4.5 per cent gelatin-salt solutions

greater for the thiocyanate than for the chloride ion. The viscosity data show that the viscosity of gelatin-potassium thiocyanate sols was less than that of gelatin-potassium chloride sols by about 3 per cent over the range of salt concentrations; consequently this factor cannot account for the peculiarity in the case of potassium thiocyanate sols. A possible explanation may be obtained by assuming that the thiocyanate ion is more strongly adsorbed on the gelatin micellae than the chloride ion and consequently fewer ions are left free to act in the conduction process. The ions adsorbed, of course, are not completely bereft of conducting ability, for upon adsorption they would then possess the velocity of the gelatin particles. This, however, is appreciably lower than for the simpler inorganic ion. Adsorption of ions would, however, increase the charge on the colloidal particle, and this would tend to increase the velocity of the particle. Thus it is

necessary to assume that adsorption has not proceeded to such an extent that the mobility of the colloidal particles has become equal to ionic mobility.

CONCLUSIONS

The fact that the change in electrical conductivity with time in the sol-gel transformation is gradual and regular is in agreement with other data on this transformation (19, 23, 4). This leads to the conclusion that the process involved in the formation of the gel structure is not a discontinuous one, such as crystallization would require, but is a gradual coagulation of particles. When gels were caused to set rapidly at low temperature, they melted more readily than those which set slowly, which may be due to the fact that the process of building up chains of particles had not proceeded to completion. It is probable that the two phases present in the gel state are not greatly different from those present in the sol state. The micellae as one phase are richer in gelatin content than the intermicellar phase. According to Bungenberg de Jong (8) the charge and hydration of the particles are not uniformly distributed over the surface of each particle but are localized in different areas. Removal of either charge or hydration would result in gel formation.

It appears probable that gelatin micellae are the chief conductors of the current in the system ash-free gelatin-water. The small decrease of conductance upon gelation is interpreted as meaning that the liquid phase is still continuous in the gel state, the process of conduction changing from cataphoresis to electroendosmosis. In order to account for the rigidity of the gel, it is assumed that the gelatin phase is also continuous. The conductivity data therefore, in our judgment, support the fibrillar theory of gel structure.

The identity of conductance of the various salts contained in the sol and gel states of gelatin also indicates that the gel structure cannot be of the discontinuous phase or honeycomb type. It is evidence again for a structure of the fibrillar type, in which the spaces between the fibrils are of sufficient size to allow the ions to travel with nearly the same freedom in the gel as in the sol state.

The decrease in the conductance of salts, owing to the presence of the gel-forming substance, is probably due to several factors. The most important of these, we believe, are adsorption of ions by the gel-forming substance and the increased resistance or increase in length of path that the ions must take, owing to the presence of the relatively huge gelatin micellae.

SUMMARY

1. The electrical conductance of ash-free gelatin in both the sol state and the gel state has been determined at 25°C. and at 30°C. Conductance

measurements were also carried out during the sol-gel transformation at constant temperature. In the cases studied, no abrupt change in conductance is observable when gelation takes place. There is, however, a gradual decrease in conductance during gelation, the maximum decreases in conductance lying between 4 and 8 per cent.

2. The electrical conductance of potassium chloride and of potassium thiocyanate over a considerable range of concentrations, when present in gelatin sol and gel, has been determined at several constant temperatures. The conductance of the electrolyte is appreciably lower in the presence of gelatin, but is approximately the same in the sol and the gel state, save at very dilute concentrations of electrolyte. Potassium thiocyanate shows a relatively greater decrease in conductance in the presence of gelatin than does potassium chloride.

3. Our results are interpreted as evidence for (a) the fibrillar structure of gelatin gels and (b) the greater adsorption of thiocyanate ion than of chloride ion by gelatin.

REFERENCES

- (1) ARRHENIUS: Brit. Assoc. Advancement Sci. Rept. **56**, 544 (1906).
- (2) BACHMAN: Z. anorg. Chem. **73**, 125 (1925).
- (3) BACHMAN AND ZSIGMONDY: Kolloid-Z. **11**, 150 (1912).
- (4) BOGUE: J. Am. Chem. Soc. **44**, 1313 (1922).
- (5) BRADFORD: Biochem. J. **12**, 351 (1918); **14**, 91 (1920); **15**, 853 (1921).
- (6) BURTON: Physical Properties of Colloidal Solutions, 2nd edition, p. 143. Longmans, Green and Co., London (1923).
- (7) COPISAROW: Kolloid-Z. **44**, 319 (1928).
- (8) DEJONG: Z. physik. Chem. **130**, 206 (1927).
- (9) DUMANSKI: Z. physik. Chem. **60**, 563 (1907).
- (10) EDSON AND REXROTH: Engineering Thesis, University of Kansas, 1928.
- (11) GREENBERG AND MACKEY: J. Gen. Physiol. **15**, 161 (1930).
- (12) HARRISON: J. Soc. Dyers Colourists **32**, 40 (1916).
- (13) HATSCHKE: Trans. Faraday Soc. **12**, 17 (1916-17).
- (14) INDEKING: Wied. Ann. **37**, 172 (1889).
- (15) JONES AND JOSEPH: J. Am. Chem. Soc. **43**, 1095 (1921).
- (16) KATZ AND ROBINSON: Kolloid-Beihefte **9**, 1 (1918).
- (17) KRUYT: Colloids, 1st edition, p. 217. John Wiley and Sons, Inc., New York (1927).
- (18) LAING AND MCBAIN: J. Chem. Soc. **117**, 1506 (1920).
- (19) OLSON: J. Phys. Chem. **36**, 529 (1932).
- (20) PROCTOR: J. Chem. Soc. **106**, 317 (1914).
- (21) SCHERRER: Nachr. kgl. Ges. Wiss. Göttingen, p. 26 (1918).
- (22) TAFT AND MALM: J. Phys. Chem. **42**, 1187 (1938).
- (23) WALPOLE: Kolloid-Z. **13**, 241 (1913).
- (24) YABUKI: J. Biochem. **8**, 157 (1928).

STUDIES ON THE LYOTROPIC SERIES. II

THE ADSORPTION OF SALTS ON GELATIN

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I. INTRODUCTION

In a previous paper (15) the lyotropic action of electrolytes on the properties of hydrophilic colloids was discussed. Experiments on the adsorption of salts on methylcellulose and on the influence of salts on the solubility and on the sol-gel transformation of methylcellulose showed that the ions at the beginning of the lyotropic series, which are strongly adsorbed, have liquefying or peptizing properties, whereas the ions at the end of the series, which are weakly or, in fact, negatively adsorbed, have solidifying or precipitating properties (12). This behavior can be interpreted in terms of Katz' theory (20, 21), according to which we have to distinguish in lyotropic action between an adsorption effect and a salting-out effect, the former being prevalent with the weakly hydrated ions at the beginning of the series, the latter with the strongly hydrated ions at the end of the series. The usual series are for the anions

CNS^- , I^- , Br^- , NO_3^- , Cl^- , acetate, tartrate, SO_4^{--}

and for the cations

Li^+ , Na^+ , K^+ , Rb^+ , Cs^+

It is desirable to extend this investigation to gelatin, because the lyotropic influence is most pronounced in this system.

There have been many investigations on the influence of acids, bases, and salts on the swelling and on the precipitation of proteins, but very few on the adsorption of salts on isoelectric gelatin. Brief mention may be made of the lyotropic series in relation to the swelling of gelatin. It was in connection with this phenomenon, amongst others, that Hofmeister (17) first obtained an order of the effectiveness of ions. Whereas he measured swelling as the quantity of liquid taken up by the gel, the measurements of Freundlich and Gordon (5) were concerned with the determination of a thermodynamically reversible property, namely, the

swelling pressure. They investigated isinglass, a substance which is probably identical with collagen, and the following series was found: $\text{SO}_4^{--} < \text{F}^- < \text{Cl}^- < \text{NO}_3^- < \text{I}^- < \text{CNS}^-$. Most authors are agreed that the swelling process is a very complex one (22, 5).

A process like the solubility or peptization of gelatin in salt solutions seems to be easier to interpret than swelling, but not many investigations of such processes are available in the literature. The next approach is the investigations of Wo. Pauli (26) on the influence of salts on the setting and the melting point of gelatin. He found a series very similar to that which was found later for the swelling pressure. The melting point was raised according to the series $\text{SO}_4^{--} > \text{tartrate} > \text{acetate}$, and lowered according to the series $\text{Cl}^- < \text{NO}_3^- < \text{Br}^- < \text{I}^-$.

Adsorption of salts on gelatin has been determined in a few cases (25, 4, 1),¹ but no systematic investigation, which allows a comparison between various salts, is available.

It was the purpose of this investigation to measure the adsorption of various salts on gelatin, and also the influence of these salts on the peptization of gelatin in water, in order to test the applicability of the theories put forward for an explanation of the lyotropic action.

II. THE GELATIN

It was desirable to carry out the investigation with absolutely dry gelatin. Drying was effected in an electrically regulated oven at 100° to 110°C., constant weight being obtained after about 40 hr. This gelatin was used for most adsorption measurements. A number of experiments were carried out with undried gelatin also, which contained approximately 15 to 16 per cent of water, due allowance being made for this water content in the calculations of the adsorption.

It was found that adsorption was in nearly all cases the same, no matter whether dried or undried gelatin was employed. The physical properties of the material were, however, very considerably altered by the drying operation. The dried gelatin was no longer easily soluble in hot water—it dissolved only partially after prolonged treatment for several days with water—nor did it swell to the same extent as the undried material. In short, the drying operation made the gelatin more similar in properties to collagen. Hofmeister (19) observed as early as 1871 that gelatin was “converted” into collagen by heating to 130°C. Other authors prefer to call the insoluble dried gelatin “pseudocollagen.” This distinction is, however, most probably immaterial, since most investigators are today agreed that collagen is not chemically different from gelatin, and that the different physical properties are due rather to a difference in micellar

¹ The experiments of these authors were carried out in mixtures of water and alcohol. A comparison of the adsorption in such mixtures with phenomena in aqueous systems is open to criticism.

and not in molecular arrangement (8, 9). The acid-binding capacity (29) and isoelectric point are the same (7) for gelatin and collagen, and the x-ray diagram of stretched gelatin is identical with that of collagen.

The insolubility of the dried gelatin simplified the experimental procedure considerably, since peptization was reduced to a minimum. With undried gelatin also the amount of peptization could be kept low by carrying out all experiments at 0°C. The peptization of undried gelatin by many salt solutions has led to the abandonment by some investigators of adsorption and swelling experiments with gelatin. The use of dried gelatin should minimize the experimental difficulties without impairing the conclusiveness of the experiments.

The material used for the experiments was "de-ashed gelatin" supplied by the Eastman Kodak Company.² It contained 15 per cent of moisture and 0.12 per cent of ash, calculated on dry weight, the ash consisting mainly of phosphates of calcium and iron; chloride and sulfate were present only in traces. This gelatin had been purified by a special process of washing at a low temperature with water at the isoelectric point, and was in flaked form. The pH was determined on a 5 per cent solution of gelatin in water and was found to be 4.7 to 4.8 by the Hellige comparator method using methyl red, and 4.8 by Michaelis' nitrophenol method using γ -dinitrophenol (1-hydroxy-2,5-dinitrobenzene). This indicated that the gelatin was isoelectric.

III. EXPERIMENTAL

A. Adsorption

Dry gelatin (6.000 ± 0.003 g.) was added to 100 ml. of the respective solution in a Jena bottle which had been previously steamed and dried. The bottle was sealed with a rubber stopper and kept for three to four days³ in a heavily lagged ice-water thermostat, during which period it was occasionally shaken. Afterwards the solution was withdrawn and analyzed. As a consequence of the swelling of the gelatin only part of the original solution was recovered, 70 to 80 ml. in the case of the dried gelatin and 60 to 70 ml. in the case of the undried gelatin.

Adsorption was determined at various concentrations of the following electrolytes:

Potassium salts.....	KCNS, KI, KBr, KCl, KNO ₃ , K ₂ SO ₄ , K ₂ C ₄ H ₄ O ₆ , KC ₂ H ₃ O ₂
Chlorides.....	KCl, NaCl, LiCl, NH ₄ Cl, RbCl, CsCl, MgCl ₂ , CaCl ₂ , SrCl ₂ , BaCl ₂ , CuCl ₂
Sulfates.....	K ₂ SO ₄ , (NH ₄) ₂ SO ₄ , MgSO ₄ , Li ₂ SO ₄ , CuSO ₄
Miscellaneous.....	LiBr, LiI

² We are very much indebted to the Eastman Kodak Company, through Dr. Lewis, for supplying us with a large quantity of this material.

³ It was ascertained that three days was a sufficient time for the attainment of equilibrium.

The salts used were the purest available, usually B.D.H. "Analar" or Merck "pro analysi." Lithium sulfate and lithium chloride were prepared from pure lithium carbonate, and cesium chloride from cesium nitrate. Cesium nitrate and rubidium chloride were only of Merck's ordinary "pure" quality. Thiocyanates, iodides, and bromides were analyzed by the Volhard method, and copper salts by the iodimetric method. The ammonium salts were determined by adding excess sodium hydroxide solution to an aliquot of the solution, then boiling off the ammonia, and titrating the excess alkali with standard acid. The remaining salts were determined gravimetrically by evaporating a weighed amount of solution, converting to the sulfate, and igniting at 610°C. to constant weight. The Mohr method for chlorides was found unsatisfactory, as a small quantity of dissolved gelatin or its decomposition products in the solution interfered with the sharpness of the end point, owing to the peptizing action of traces of such substances on silver chloride. The

TABLE 1
pH values of various solutions after adsorption

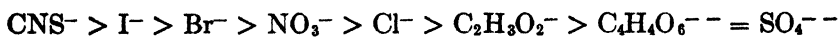
SOLUTION	pH	SOLUTION	pH
Water.....	4.6	M/4 MgCl ₂	4.8
2 M KCl.....	5.2	M/4 CaCl ₂	4.8
M/3 KBr.....	5.1	M/4 SrCl ₂	4.9
M/10 KC ₂ H ₃ O ₂	5.9	M/4 BaCl ₂	4.9
M/5 K ₂ SO ₄	5.3	M/2 (NH ₄) ₂ SO ₄	5.2
M/4 LiCl.....	4.9	M/5 CuCl ₂	4.4
M/4 NaCl.....	4.9		

above gravimetric method gave more reproducible results. Blank determinations with distilled water gave only a small quantity of soluble impurity, *viz.*, 0.003 g. per 100 g. of solution, and this correction was applied to each gravimetric analysis.

The pH values of various solutions were measured before and after adsorption, by comparison with the Michaelis nitrophenol standards (table 1). With the exception of potassium acetate the pH of the solutions after adsorption was usually between 4.5 and 5.5, *i.e.*, fairly near that of the isoelectric gelatin. Potassium acetate remained more alkaline (pH = 5.9). Obviously small amounts of dissolved gelatin or of decomposition products in the solutions after adsorption determine the pH. There is no evidence of appreciable hydrolytic adsorption.

The adsorption values were calculated and tabulated in the same way as in the previous publication. The apparent adsorption $a = c - c'$, where c and c' are molar concentrations before and after adsorption, is plotted against the molar equilibrium concentration (c'). Circles denote

experiments with dried gelatin, triangles those with undried gelatin. In general, the anions exhibit a greater range of adsorption than do the cations. With the acid radicals there is a very wide range from strong positive to strong negative apparent adsorption. With the potassium salts the order is:



thiocyanate and iodide ion showing positive apparent adsorption at all concentrations, tartrate and sulfate ion exhibiting strong negative apparent

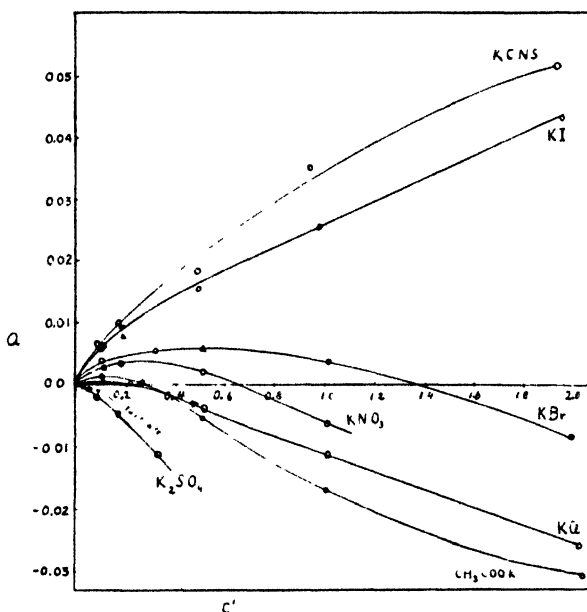
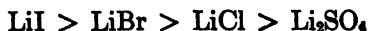


FIG. 1. Plot of apparent adsorption, a , against molar equilibrium concentration, c' . O, experiments with dried gelatin; Δ , experiments with undried gelatin.

adsorption (figure 1). This means, of course, that the true adsorption of sulfate and tartrate is either zero or, more probably, very small, whereas that of the ions at the beginning of the series is fairly large. The curves of apparent adsorption have the usual form. For the more strongly adsorbed salts they are convex upwards, i.e., the percentage adsorption diminishes arithmetically with concentration, often being at first positive then becoming negative. Some curves indicate a point of inflection at higher concentration, i.e., they tend to approach the abscissa. This is to be expected, since the relative effect of the amount adsorbed will become less when the concentration increases (cf. 15). The curves of the very strongly negatively adsorbed salts show an inclination towards an

asymptotic approach to the zero concentration. A comparison with the curves of more strongly adsorbed salts suggests that even with sulfates, which exhibit the strongest negative adsorption, the true positive adsorption is probably not zero (cf. section IV A). The order of the various ions in some cases varies with increasing concentration; the curves for chloride and acetate ions intersect at low concentration, but the difference in the adsorption values is not very great.

The lithium salts show the same order as the potassium salts



each being more strongly adsorbed than the corresponding potassium salts (figure 2).

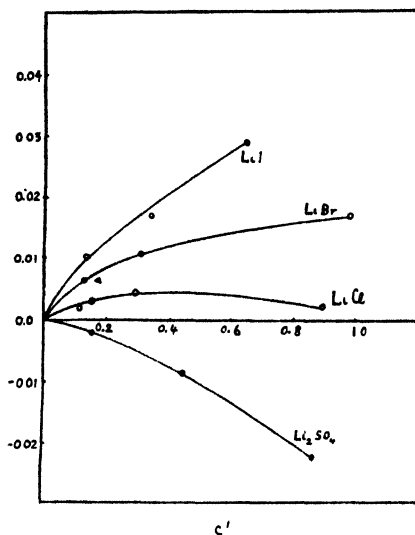


FIG. 2

FIG. 2. Plot of apparent adsorption, a , against molar equilibrium concentration, c' , for lithium salts. \circ , experiments with dried gelatin; Δ , experiments with undried gelatin.

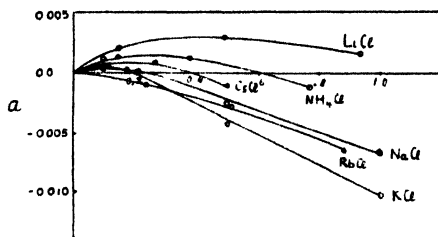
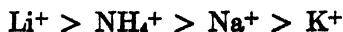


FIG. 3

FIG. 3. Plot of apparent adsorption, a , against molar equilibrium concentration, c' , for alkali-metal chlorides.

With the cations there is less separation between the magnitudes of adsorption. The order of the univalent chlorides is



The positions of rubidium chloride and cesium chloride are obscure. They lie between potassium chloride and ammonium chloride, contrary to expectations (figure 3).

The isotherm of magnesium chloride is very similar to that of lithium chloride, whereas the other alkaline-earth chlorides are more strongly adsorbed (figure 4), the order being



The gelatin in barium chloride solutions—contrary to all other cases—becomes turbid. The adsorption in this case does not seem to be as completely reversible as in all the other cases. After washing the gelatin with distilled water until no more chloride ion could be extracted, there remained an ash content of 0.16 per cent, as compared with 0.030 per cent of the original gelatin.⁴ It can be easily shown that this increase in ash content cannot be accounted for by a reaction of barium chloride

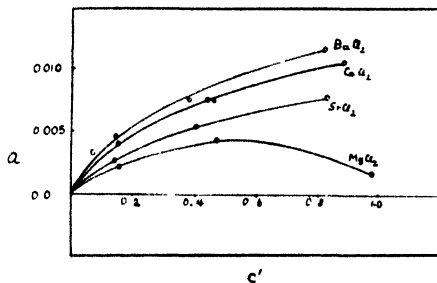


FIG. 4

FIG. 4. Plot of apparent adsorption, a , against molar equilibrium concentration, c' , for alkaline-earth chlorides.

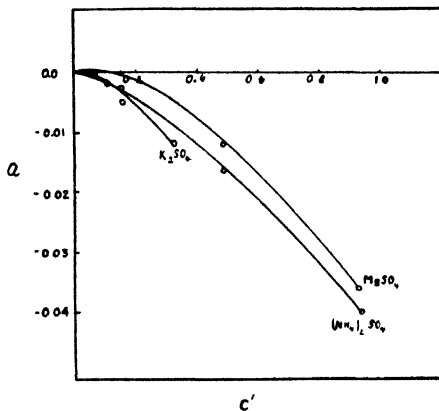


FIG. 5

FIG. 5. Plot of apparent adsorption, a , against molar equilibrium concentration, c' , for sulfates of potassium, magnesium, and ammonium.

with the ash of the gelatin (calcium phosphate). With the alkali-metal salts and with copper salts, on the other hand, the adsorption proved to be completely reversible. In an experiment with potassium thiocyanate the solution added to the dried gelatin contained 0.1998 equivalent. If the gelatin was washed ten times with distilled water, the combined wash waters plus the equilibrium solution contained 0.1993 equivalent.

Strong negative adsorption is shown by the sulfates (cf. 4) of the alkali and alkaline-earth metals (figure 5). The isotherms lie fairly close together.

In contrast to its negative adsorption on methylcellulose, copper sulfate

⁴ A gelatin from a different batch, which contained less ash, was employed in this as well as in some other experiments.

is very strongly adsorbed on gelatin (figure 6). The curves may, however, not represent purely the adsorption and may be blurred by the Donnan effect (cf. section IV C).

Generally, adsorption on undried gelatin did not give results deviating from those obtained with dried gelatin, provided that in the calculations due allowance was made for the water content of the gelatin. Noticeable deviations occurred only with copper salts; very slight deviations, found in the case of potassium thiocyanate, are almost within the limit of analytical error. Apart from the figures mentioned above, this is also shown in figure 7, representing experiments with a new batch of gelatin, which

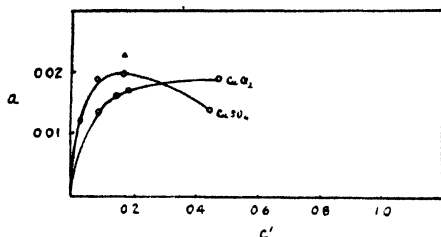


FIG. 6

FIG. 6. Plot of apparent adsorption, a , against molar equilibrium concentration, c' , for cupric chloride and cupric sulfate. \circ , experiments with dried gelatin; Δ , experiments with undried gelatin.

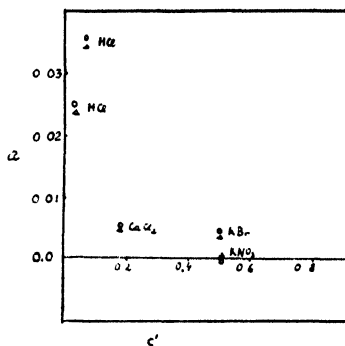


FIG. 7

FIG. 7. Plot of apparent adsorption, a , against molar equilibrium concentration, c' , for hydrochloric acid, calcium chloride, potassium bromide, and potassium nitrate, using a new batch of gelatin. \circ , experiments with dried gelatin; Δ , experiments with undried gelatin.

showed the adsorption of the various electrolytes in the same order as the old one but with slightly different absolute values.

B. "Solubility"

In most systems lyotropic action is shown very clearly with regard to solubility, therefore the solubility of gelatin in various salt solutions at 20°C. was determined. One gram of undried gelatin was added to 100 ml. of the solution in a 150-ml. bottle. Each solution was made by dissolving the salt in water so that the concentration was 0.25 mole of the salt in 1000 g. of water. Thus the electrolyte was in every case the same molar fraction. The bottles were then shaken in a thermostat at 20°C. for 36 hr. After the settling of the gelatin the supernatant liquid was filtered off through a cotton wool pad packed in a constricted glass tube connected

to a vacuum pipet. The gelatin in these solutions was analyzed by nitrogen determinations according to Kjeldahl, the nitrogen content of the gelatin used being 18.04 per cent per dry weight. The method was standardized by determinations on acetanilide and blanks run on cane sugar. Since thiocyanates and nitrates contain nitrogen, the solubility of the gelatin in these solutions was determined by evaporating to dryness a weighed amount of filtrate, drying at 110°C. to constant weight, then converting into sulfate. The gelatin was then removed by ignition, and the percentage of dissolved gelatin could be computed by comparing the weight of the mixture of nitrate plus gelatin (constant at 110°C.) with that of the sulfate after the gelatin had been ignited. Table 2 shows the

TABLE 2
Solubility of gelatin in various salt solutions at 20°C.

SOLUTION	SOLUBILITY	SOLUTION	SOLUBILITY
	<i>mg. per 100 grams</i>		<i>mg. per 100 grams</i>
Potassium salts:		Alkali chlorides:	
KCNS.....	373	LiCl ..	70
KI.....	257	NaCl...	69
KNO ₃	145	KCl ..	69
KBr ..	78	Alkaline-earth chlorides:	
KCl ..	69	MgCl ₂ ..	85
K ₂ SO ₄	41	CaCl ₂ ..	104
KC ₂ H ₃ O ₃	38	SrCl ₂ ..	174
Lithium salts:		BaCl ₂	240
LiI.....	182	Miscellaneous:	
LiBr.....	123	MgSO ₄	38
LiCl ..	70	H ₂ O.....	51
Li ₂ SO ₄	41		

solubilities of gelatin in milligrams per 100 g. The solubility of gelatin in distilled water is 51.4 mg. in 100 g. at 20°C.

The results for the solubility are only approximate. The accuracy is of the order of a few per cent, the discrepancies increasing with increasing solubility. This is not due to an analytical error, as the nitrogen determinations on acetanilide and on the original gelatin showed. The difficulty lies in the separation of the swollen gelatin gel from the solution after the shaking operation at 20°C. On filtration minute fragments of the swollen gelatin may be forced through the filter medium because of their plastic nature. In addition, slight changes in temperature may affect the results considerably, since the "solubility" of gelatin increases enormously in the temperature range between 18°C. and 22°C. Below this range gelatin is practically insoluble; above it, its solubility soon

becomes very high. Both these factors would lead to high results; therefore in the table the least value in any particular solution was taken as the nearest approach to the correct value.

From the results it is seen that the solubility of gelatin is increased by the following cations in the order $\text{CNS}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^-$, and is decreased by SO_4^{--} and to a slightly larger degree by the acetate ion. The order is identical for the potassium and the lithium salts.

The chlorides of the alkali metals lithium, sodium, and potassium increase the solubility to approximately the same extent. Thus, contrary to expectations, no lyotropic influence is noticeable with the alkali-metal salts.

Magnesium sulfate, like other sulfates, diminishes the solubility.

The alkaline-earth chlorides greatly increase the solubility of the protein in the order



the solubility in the barium chloride solution being almost as high as that in a potassium iodide solution of the same concentration.

IV. DISCUSSION

A. *The hydration of gelatin*

If it be assumed that ammonium sulfate and magnesium sulfate, which show the strongest negative adsorption of all electrolytes under investigation, are not actually adsorbed, i.e., that the negative apparent adsorption is due entirely to the water being taken up by the adsorbent, it is possible to calculate approximately the hydration of the gelatin. The greatest negative apparent adsorption is found with *M*/1 magnesium sulfate and *M*/1 ammonium sulfate (cf. figure 5) to be of the order of 4 per cent. The amount of water adsorbed by 6 g. of gelatin from 100 ml. of solution is therefore 4 g. Thus the hydration at 0°C. becomes about 60 to 70 per cent, calculated on the dry weight. This represents a minimum value, as the above-mentioned sulfates may show slight positive adsorption. Moreover, at room temperature and in the absence of salt, the hydration of gelatin may be different. Since the curves for the dried gelatin (pseudo-collagen) coincide with those for the undried gelatin, we may assume that both are hydrated approximately to the same amount.

Corresponding values for the hydration of gelatin obtained by other methods are: (1) 55 per cent, from the amount of water that cannot be frozen in the jelly (23); (2) 44 to 51 per cent, from the amount of water that is not free to hydrate cobaltous chloride (10); (3) 50 to 55 per cent, from the minimum amount of water present in the gelatin, which causes the volume contraction on swelling in water to be reduced to zero (14).

B. Adsorption

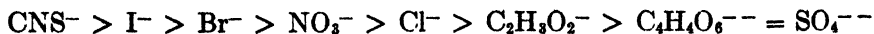
The contraction of the total volume which occurs when gelatin swells or dissolves in water is evidence that water is adsorbed by the gelatin. The water of this hydration layer has a higher density than the free water. Thus the adsorbed water is under a high internal pressure, which is due to the polarizing effect of the polar groups of the protein molecule on the water dipoles. If also a solute be present, the adsorbed water may no longer act as a solvent. If little or no solvent is adsorbed by the gelatin particles, the concentration of the solution will increase and negative apparent adsorption will result. However, in most cases at least, the electrolyte is, in fact, also adsorbed by the gelatin; otherwise zero or positive adsorption would be impossible. The adsorbed electrolyte will modify the properties of the gelatin. It may do this itself or through the extra water of hydration (the ions of the electrolyte being hydrated) which it carries onto the protein, tending to increase its dispersion. This is the *direct* effect. The solute not adsorbed also has an effect which is *indirect*, in that the ions in solution will enter into competition with the colloidal particles for the (osmotic) water at their disposal.

The direct (adsorption) effect is that proposed by Katz (20, 21) to explain the lyotropic action in the cases of "salting in" (i.e., increase of solubility) by iodides and thiocyanates. The indirect effect is the "salt-ing-out" effect (i.e., decrease of solubility), well known from the investigations of Hofmeister (17).

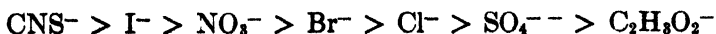
The (indirect) salting-out effect operates at all times, the influence being more pronounced with increasing concentration. If no salt, or very little, is adsorbed, then mainly this effect operates. This is shown by the magnesium, potassium, and ammonium sulfates, which show strong negative adsorption. They all depress the solubility of gelatin; moreover they are well-known protein precipitants.

The (direct) salting-in effect is evident with the increase of solubility of gelatin in solutions of thiocyanates and iodides. These salts show strong positive adsorption. The adsorbed ions carry with them their water of hydration, which has a "liquefying" or "dispersing" effect on the protein.

The order of adsorption is:



which may be compared with the order of the influence on the solubility, *viz.*,



The negatively adsorbed sulfates and acetates depress the solubility of gelatin. On the other hand, the strongly adsorbed iodides and thiocyanates increase the solubility by several hundred per cent.

There is fair agreement between the two series, thus supporting Katz' theory. The series with regard to adsorption also agrees well with that obtained by Freundlich and Gordon (5) for the swelling pressure of isinglass. With regard to the interchange of nitrate and bromide it may be pointed out that it occurs also in some other phenomena, e.g., the influence of salts on the "melting point" of methylcellulose (12) and on the shrinking of collagen (21), the order in both cases being:



The chlorides of the univalent metals show increasing adsorption on gelatin according to the series



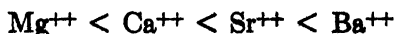
This does not, however, make itself felt with the solubility of gelatin in solutions of these metals, since the solubility is the same in all the three cases.

The influence of the alkali cations on the swelling pressure of collagen (isinglass) is opposite to expectations, the strongly adsorbed lithium chloride depressing the swelling pressure strongly and more than the weakly adsorbed potassium chloride (5). In the case of the anions, on the other hand, the strongly adsorbed thiocyanate and iodide show, as would be expected, a strongly increasing effect on the swelling pressure (π). The discrepancy with regard to the cations may, however, disappear if the swelling pressures at low concentrations (c), for instance, at unit concentration (π_0) be compared. The slope of the $\log \pi$ - $\log c$ curves is different for the three salts lithium chloride, sodium chloride, and potassium chloride, the exponent (K) in the Freundlich-Posnjak equation (6)

$$\pi = \pi_0 \cdot c^K$$

varying from 2.9 to 4.0. An extrapolation of the $\log \pi$ - $\log c$ curves to low concentrations would make the curves intersect and thus reverse the order of the swelling pressures. Since, for experimental reasons, the swelling pressures have to be measured at high concentrations of the jelly, Freundlich and Gordon have not extrapolated their π values to π_0 , because of the uncertainty of such an extrapolation.

The bivalent alkaline-earth chlorides increase the solubility in the order



This is not quite the order of adsorption, which is



still Mg^{++} and Ba^{++} are antipodes in both cases. However, the difference in adsorption between Ca^{++} and Sr^{++} is only slight.

The lyotropic series obtained for the adsorption of the anions agrees on the whole with the order expected from the hydration of the ions and from their influence on other phenomena. The adsorption increases with decreasing energy of hydration, at least so far as the hydration values are known (cf. 15). The same applies to the alkaline-earth ions, where the amount of hydration decreases from Mg^{++} to Ba^{++} (31), the relative values being 14 (Mg^{++}), 10 (Ca^{++}), 8 (Sr^{++}), and 4 (Ba^{++}). The adsorption, in accordance with expectations, increases from magnesium to barium.

The alkali cations, on the other hand, show the opposite behavior. Here the adsorption increases from potassium to lithium, i.e., with increasing hydration of the ion, the relative hydration numbers being 5.4 (K^+), 8.4 (Na^+), 14 (Li^+). This behavior is opposite to what would be expected on the basis of the discussion in our previous publication, and we are not able at present to provide an explanation for this anomaly. However, as pointed out previously, the energy of hydration is only one factor determining the adsorption of an ion. The second factor is the specific affinity between the ion and the adsorbent, which is in the present case very difficult to assess.

Copper salts, like hydrochloric acid, are bound to a very great extent at low concentration, the percentage adsorption here⁵ being greater than with other salts (cf. figure 6). It is of interest to note that the maximum combination of cupric chloride and cupric sulfate is a little greater than 0.04 equivalent for 6 g. of gelatin. The combining power for hydrochloric acid is approximately 0.045 equivalent per 6 g. of gelatin. This similarity indicates a stoichiometrical relation and suggests a chemical nature of the adsorption process in the case of these electrolytes, thus supporting Northrop's and Kunitz' experiments and conclusions (24). Heavy-metal combinations with proteins have been demonstrated in many cases (cf. 16, 25, 27, 28). Also with alkali and alkaline-earth salts, the nature of the adsorption may be due to a chemical interaction between the ions of the salt and the respective groups of the protein ampholyte



However, the heat of combination is very small indeed (13).

Another possible type of combination is that consequent upon the

⁵ The isotherms of the copper salts are initially much steeper than those of the other salts.

hydrolysis of the salt, whereby either the acid or the base produced, or both, may be adsorbed. This actually occurs with some heavy-metal salts, e.g., ferric chloride and aluminum chloride, as demonstrated by the strong *negative* heat of the processes in these cases (13). The negative heat is due to the hydrolysis of these salts. No evidence, however, for a hydrolytic adsorption was found in the case of alkali and alkaline-earth salts, the pH after adsorption being virtually that of the isoelectric gelatin. Moreover, no negative, but a small positive, heat was found with alkali and alkaline-earth salts (13).

C. Donnan equilibrium

In all cases in which reactions of protein jellies with electrolytes are investigated, the possibility of Donnan equilibrium effects must be taken into account. If one of the ions of the electrolyte C^+A^- be more strongly adsorbed than the other, e.g., the metal ion (C^+), an ion GC^+ (G = gelatin) may be formed, which, being part of the jelly, is not diffusible. This will result in an unequal distribution of the electrolyte C^+A^- between jelly and solution, its concentration in the solution being higher than in the jelly. In our adsorption experiments the electrolyte concentration in the free liquid is measured, and the apparent adsorption is calculated from the difference between the concentration of the original and that of the free liquid (outside the gel) after the establishment of equilibrium. It is tacitly assumed that the concentration of the free, i.e., not adsorbed, electrolyte is the same in the imbibed and in the free liquid. As a consequence of the Donnan effect, however, the concentration of the free liquid outside the gel may be larger than that of the imbibed liquid, and therefore the apparent adsorption, as calculated in this way, will appear to be smaller than it really is.

A Donnan correction, however, will be appreciable only if two conditions are *simultaneously* fulfilled:

(1) Appreciable positive true adsorption. Where there is zero or negative apparent adsorption, no Donnan correction need be expected. (2) Unequal adsorption of cation and anion. Of the investigated electrolytes, potassium thiocyanate, potassium and lithium iodides, and the copper salts are fairly strongly adsorbed, but only in the case of hydrochloric acid and of the copper salts is there evidence for an appreciable unequal adsorption of cation and anion. This was inferred by Northrop and Kunitz (24) from the determination of the membrane potential. For alkali-metal salts no such effects were found. It is true that some alkali-metal salts alter the isoelectric point of proteins, but this may be due merely to the influence of interionic forces on the respective dissociation equilibria, and thus is not sufficient evidence for the existence of unequal adsorption of anion and cation. Hence an appreciable Donnan effect is

improbable even with strongly adsorbed salts, like thiocyanates and iodides.

It would, of course, be desirable to determine experimentally whether a Donnan effect exists in the case of the more strongly adsorbed ions. Procter and Wilson (30), in their experiments on the system gelatin-hydrochloric acid, determined the hydrochloric acid concentration in the imbibed liquid by de-swelling the swollen jelly in a concentrated salt solution. Such a procedure is feasible in the system gelatin-hydrochloric acid, since no displacement of the chemically bound hydrochloric acid by the salt need be feared. In our case, however, a displacement of the adsorbed salt by the salt of the concentrated de-swelling solution may easily occur, and therefore this procedure would give misleading results.

It was found with the strongly adsorbed copper sulfate that the equilibrium concentration in the free liquid was slightly different when undried gelatin was used instead of the dried material. Also the amount of swelling is different. In the first case only 20 to 30 ml., in the second case 40 to 50 ml. (of the total 100 ml.) was imbibed. A discussion of the effect of the amount of swelling on the equilibrium concentration in the free liquid (at constant total volume of the system) on the basis of the elementary theory of the Donnan equilibrium (2) shows that the concentration of the free liquid, and thus the calculated apparent adsorption, are not appreciably influenced by the ratio of free liquid to imbibed liquid. Thus it would appear at the outset that the difference in apparent adsorption between the dried and the undried gelatin is not related to a possible Donnan effect. However, a discussion on the basis of the elementary theory assumes complete dissociation of the hypothetical colloidal electrolyte, and thus neglects the probably very appreciable decrease of the activity coefficient with increasing concentration of the hypothetical colloidal electrolyte in the jelly. Assuming that its activity coefficient varies with the degree of swelling, and considering the general condition for equilibrium,⁶

$$(f_C m_C)_g \times (f_A m_A)_g = (f_C m_C)_l \times (f_A m_A)_l$$

the concentration of the electrolyte in the free liquid will alter with varying degree of swelling. Moreover, F. G. Donnan and E. A. Guggenheim (3) have shown that a rigorous theory has to consider the ratio of the partial molar volumes of solute and solvent. This also will alter with varying degree of swelling.

Summing up, the differences in apparent adsorption of copper sulfate between dried and undried gelatin may be due to a Donnan effect, con-

⁶ f_C and f_A are activity coefficients of cation and anion, respectively. m_C and m_A are molalities of cation and anion, respectively. The indices g and l denote gel and free liquid, respectively.

sidering the rigorous theory. On the other hand, the possibility that undried gelatin, perhaps as a consequence of its looser micellar arrangement, has groups available for adsorption or chemical combination which the dried gelatin (pseudocollagen) lacks, cannot be disregarded. This would make itself felt more with a strongly adsorbed salt, like cupric sulfate, than with others which are only weakly or negatively adsorbed.

K. Hess, C. Trogus, and O. Schwarzkopf (11) investigated whether a Donnan effect existed in the equilibrium between cellulose and sodium hydroxide solution. The imbibed solution was recovered by pressing. No difference in concentration was found between the imbibed liquid and the free liquid.⁷ The adsorption of various salts on cellulose is at present being investigated in this laboratory by G. C. McKillop. It is easier in this system to determine directly the electrolyte concentration in the imbibed liquid than it is in the case of gelatin. Preliminary experiments with potassium thiocyanate reveal the absence of a Donnan effect, although the adsorption of this salt on cellulose is appreciable.

SUMMARY

1. The adsorption of various neutral salts on isoelectric gelatin has been studied and the following series obtained:

(a) Potassium salts: $\text{CNS}^- > \text{I}^- > \text{Br}^- > \text{NO}_3^- > \text{Cl}^- > \text{C}_2\text{H}_3\text{O}_2^- > \text{C}_4\text{H}_4\text{O}_6^{--} = \text{SO}_4^{--}$.

(b) Lithium salts: $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{SO}_4^{--}$.

(c) Alkali salts: $\text{Li}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{K}^+$.

(d) Alkaline-earth salts: $\text{Ba}^{++} > \text{Ca}^{++} > \text{Sr}^{++} > \text{Mg}^{++}$.

The differences between the cations is less marked than those of the alkali salts; iodides and thiocyanates show the strongest positive adsorption. Strong adsorption is also found with copper salts. The sulfates of ammonium, magnesium, potassium, and lithium show the strongest negative adsorption.

2. Experiments were carried out with undried gelatin as well as with the dried substance (pseudocollagen). With all salts, except cupric sulfate, identical results were obtained.

3. The solubility of gelatin is decreased by potassium sulfate and potassium acetate and increased by the other potassium salts in the order Cl^- , Br^- , NO_3^- , CNS^- . Magnesium, calcium, strontium, and barium chlorides increase the solubility in this order, the solubility in barium chloride solution being fairly large. Thus adsorption and solubility data show the relation that would be expected. On the other hand, contrary

⁷ The same result was obtained with sodium chloride. This experiment, however, is not quite conclusive, since, according to our experience, sodium chloride is negatively adsorbed on cellulose and therefore no Donnan effect can be expected with this salt.

to expectations, the solubility of gelatin in solutions of all alkali-metal chlorides is the same.

4. From the negative adsorption of sulfates the minimum hydration of gelatin is calculated as 0.6 to 0.7 g. of water per gram of gelatin.

5. The lyotropic action of salts on gelatin, as composed of an adsorption effect and a salting-out effect, is discussed with regard to adsorption, solubility, and swelling pressure. Like the experiments on methylcellulose, those on gelatin show that Katz' theory is generally a satisfactory basis for explanation, although a number of features still remain unexplained.

6. The possible influence of a Donnan effect on the determination of adsorption is discussed.

REFERENCES

- (1) BANCROFT, W. D., AND GOULD, L. P.: *J. Phys. Chem.* **38**, 197 (1934).
- (2) DONNAN, F. G.: *Z. Elektrochem.* **17**, 572 (1911).
- (3) DONNAN, F. G., AND GUGGENHEIM, E. A.: *Z. physik. Chem.* **A162**, 346 (1932).
- (4) DUMANSKI, A.: *Z. physik. Chem.* **60**, 559 (1907).
- (5) FREUNDLICH, H., AND GORDON, P. S.: *Trans. Faraday Soc.* **32**, 1415 (1936).
- (6) FREUNDLICH, H., AND POSNJAK, E.: *Kolloidchem. Beihefte* **3**, 517 (1912).
- (7) GERNGROSS, O., AND ST. BACH: *Biochem. Z.* **143**, 542 (1923).
- (8) GERNGROSS, O., AND KATZ, J. R.: *Kolloid-Z.* **39**, 180 (1926).
- (9) GERNGROSS, O., AND KATZ, J. R.: *Naturwissenschaften* **13**, 900 (1925).
- (10) HATSCHEK, E.: *Trans. Faraday Soc.* **32**, 787 (1936).
- (11) HESS, K., TROGUS, C., AND SCHWARZKOPF, O.: *Z. physik. Chem.* **A162**, 187 (1932).
- (12) HEYMANN, E.: *Trans. Faraday Soc.* **31**, 846 (1935).
- (13) HEYMANN, E.: *Kolloid-Z.* **50**, 97 (1930); *Trans. Faraday Soc.* **31**, 354 (1935).
- (14) HEYMANN, E.: Unpublished results.
- (15) HEYMANN, E., BLEAKLEY, H. G., AND DOCKING, A. R.: *J. Phys. Chem.* **42**, 353 (1938).
- (16) HEYMANN, E., AND OPPENHEIMER, F.: *Biochem. Z.* **199**, 468 (1928).
- (17) HOFMEISTER, F.: *Arch. exptl. Path. Pharmacol.* **24**, 247 (1888); **25**, 1 (1888); **27**, 395 (1890); **28**, 210 (1891).
- (18) HOFMEISTER, F.: *Z. physiol. Chem.* **2**, 299 (1871).
- (19) KATZ, J. R., AND MUSCHTER, F. J. F.: *Biochem. Z.* **257**, 385 (1933).
- (20) KATZ, J. R., AND WEIDINGER, A.: *Biochem. Z.* **259**, 191 (1933).
- (21) KÜNTZEL, A.: *Biochem. Z.* **80**, 187 (1917).
- (22) MORAN, T.: *Proc. Roy. Soc. (London)* **A112**, 30 (1926); **135**, 41 (1932).
- (23) NORTHROP, J. H., AND KUNITZ, M.: *J. Gen. Physiol.* **7**, 25 (1924); **9**, 351 (1926); **11**, 481 (1928).
- (24) ORYNG, T., AND PAULI, W.: *Biochem. Z.* **70**, 368 (1915).
- (25) PAULI, W.: *Pflüger's Archiv* **71**, 333 (1898).
- (26) PAULI, W., AND GOIGNER, E.: *Biochem. Z.* **235**, 271 (1931).
- (27) PAULI, W., AND MUTULA, J.: *Biochem. Z.* **80**, 187 (1917).
- (28) PROCTER, H. R.: *J. Chem. Soc.* **105**, 313 (1914).
- (29) PROCTER, H. R., AND WILSON, J. A.: *J. Chem. Soc.* **109**, 307 (1916).
- (30) WASHBURN, E. W., AND MILLARD, E. B.: *J. Am. Chem. Soc.* **37**, 694 (1915).

CHANGES IN MINERAL OIL DUE TO X-RAY OR ULTRAVIOLET IRRADIATIONS

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The amount of ionization produced by radiation in the gaseous phase can easily be measured. It is much more difficult to determine directly the ionization produced in liquids, but it can be estimated from the number of ions found in air, although the ionization potentials are different. In aqueous solutions chemical reactions of the solute may occur, and the number of molecules changed is usually of the same order of magnitude as the estimated number of ions or activated molecules (6) produced in the solution (mainly in the solvent) by the radiation. As this number of molecules is usually a very small proportion of the total number of molecules, difficulties are encountered in the measurement of the chemical changes produced.

A study of the effect of roentgen and ultraviolet rays on straight-chain saturated hydrocarbons has been carried out. A very sensitive method of determining that chemical reactions took place was first discovered and utilized (9). If a drop of the unirradiated oil is placed on a clean water surface it forms a lens occupying a certain small area. A drop of the same volume, from oil that has been irradiated in the presence of oxygen, spreads over a larger area, and the size of the interface is larger, the greater the exposure of the oil to roentgen or ultraviolet rays. It seemed evident that this was due to the formation of fatty acids or other hydrophilic types of molecules (7, 1). Drops of irradiated oil placed on a water surface spread to certain areas because some of the oxidized oil molecules go to the water-oil interface. The area covered by such an oil drop gives information concerning the quantity of hydrophilic molecules present in the oil.

The amount of different products formed is too small to permit ordinary chemical analysis to be performed with much accuracy. In order to obtain some information concerning these products the following methods have been utilized: (1) Determination of the change in the absorption spectrum in the ultraviolet region and comparison with the absorption caused by the addition of minute amounts of known compounds

to the oil. (2) A study of the behavior of oil drops on water under different conditions. (3) Determination of unsaturation and acidity by regular chemical methods.

ABSORPTION SPECTRA

A heavy mineral oil¹ having the trade name "Bacol" was irradiated by x-rays or ultraviolet light. The x-ray irradiation was carried out intermittently, the oil being irradiated by a 200 KVP, 30 milliamperes machine, with no filtration, and only during times when the machine was being used for purposes of treatment. The intensity of the radiation was 460 roentgens per minute at the position of the oil while it was being irradiated. The oil was irradiated in half-filled test tubes. Usually about 6 hr. of irradiation were given per day. A quartz mercury lamp of the Cooper-Hewitt type was used for the ultraviolet irradiation. The lamp operated at about 50 volts and 4 amperes. Except for experiments in which the oil was placed in a quartz container to be evacuated and later sealed from the atmosphere, the oil was irradiated in open Pyrex culture dishes. These dishes were about 10 cm. in diameter, contained 50 ml. of oil, and were placed 30 cm. from the arc. The most effective part of the ultraviolet spectrum in producing chemical changes in the oil is below 2800 Å., although changes in the composition of the oil due to irradiation by sunlight have been observed.

Absorption curves were obtained by means of a Judd-Lewis sector-photometer and a Hilger spectrograph. The continuous spectrum of a hydrogen arc was used as a light source. The absorption spectra were usually determined about 24 hr. after the irradiation. No changes in the absorption, as a function of the time since irradiation, were noted. An absorption spectrum of unirradiated oil used in these experiments, after the oil had been filtered through properly prepared fuller's earth, is shown as curve A of figure 1. The filtration decreases considerably the absorption in all regions, but cannot reduce the maxima at 2700 Å. much beyond that shown in the figure. The extinction coefficient, $K = 1 \log_{10} I_0/I$, at these maxima changed from approximately 2 before the filtration to about 0.6 after filtration. This absorption band is probably due to impurities in the oil. These impurities have little effect on the products formed by irradiation, as the measured changes were the same whether or not the oil had been purified by filtration. When absorption work was carried out it was necessary that the initial absorption of the oil be as small as possible, so as not to mask the effects of irradiation.

¹This oil is also known as "Medicol 4A" and may be obtained from the Sherwood Petroleum Company, Minneapolis, Minnesota. The oil has a viscosity (Saybolt) of 315 to 325 at 100°F. and a density of 0.882 to 0.892, and conforms to U. S. Pharmaceutical standards.

Curves showing the change of absorption of the oil due to irradiation with x-rays and ultraviolet light are given in figures 1 and 2, respectively. The curves indicate that the amount of material formed is not a simple function of the quantity of radiation incident upon the oil, but that the

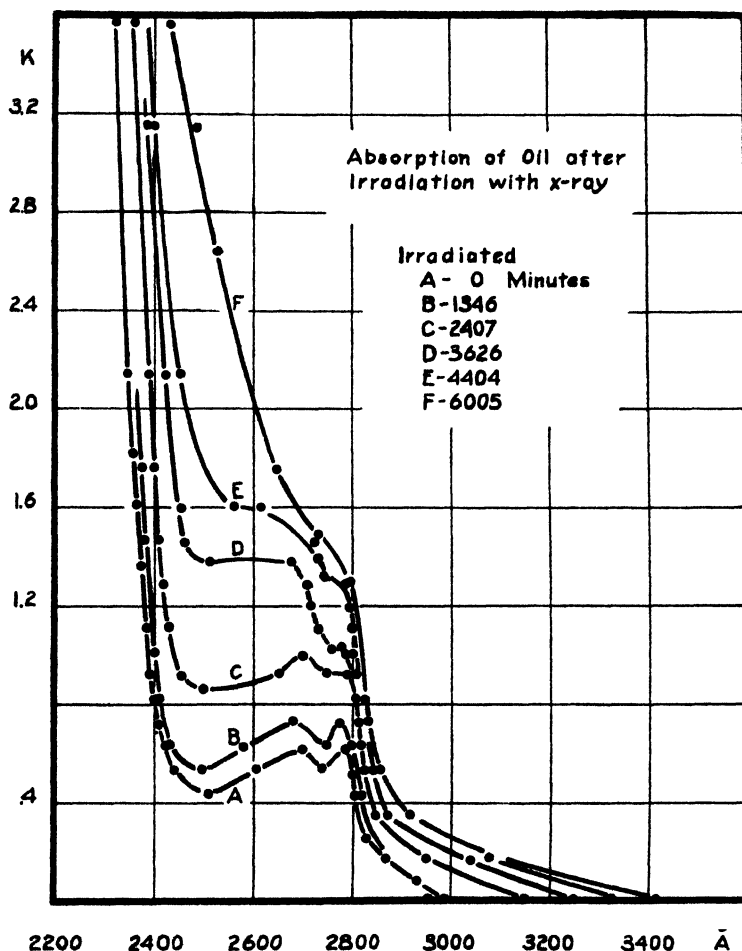


FIG. 1. Absorption curves of oil that has been irradiated with x-rays, 200 KVP and 30 milliamperes, 460 roentgens per minute. The oil was contained in half-filled stoppered test tubes while irradiated.

quantity forms with increasing rapidity for the first periods of time and, in the case of the ultraviolet irradiation, approaches saturation. The effective quantity of x-ray dose was not as great as that of ultraviolet, and the time of irradiation was longer. No saturation appears in this case within the range of exposure used. The dose of x-rays needed for a

measurable change in absorption is about 60 kiloroentgens, which is very large. Of the many reactions taking place some, evidently, are chain reactions. The decrease in the rate of change of absorption, after long periods of irradiation, is attributed to the depletion of the absorbed oxygen in the oil and to polymerization of some of the unsaturates formed.

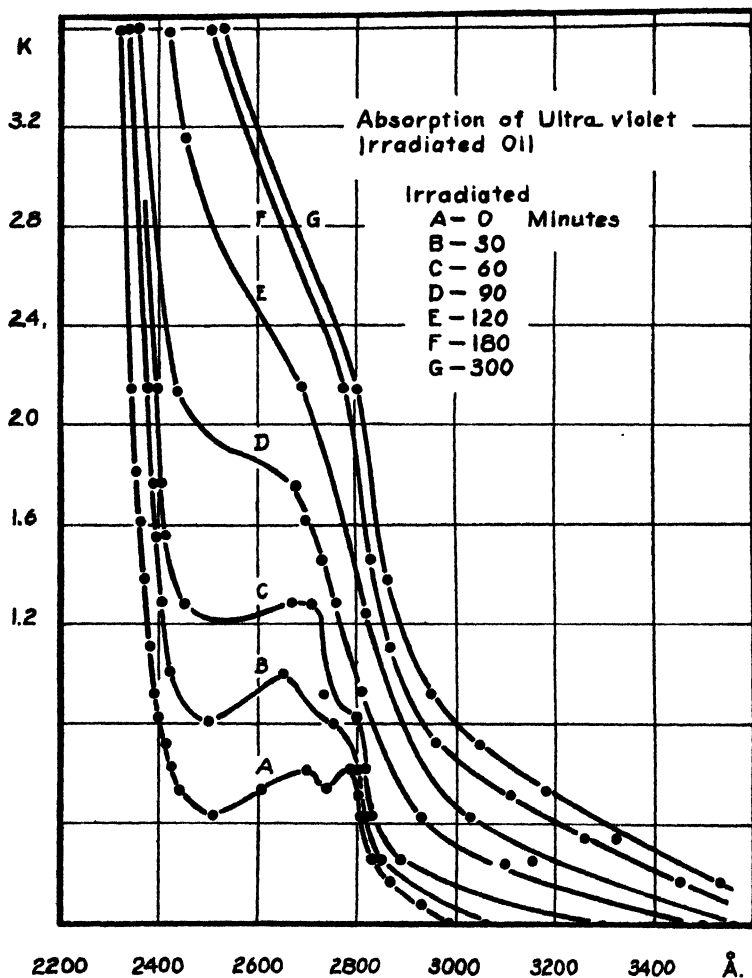


FIG. 2. Absorption curves of oil irradiated by ultraviolet while in open Pyrex culture dishes.

In order to determine the effect of different gases above the oil and absorbed in the oil during irradiation, the oil to be irradiated was placed in a quartz cell about 4 in. long and 0.5 in. in diameter. The cell contained about half its volume of oil. This cell containing the oil was evacuated

for several hours and the desired gas,—carbon dioxide, nitrogen, hydrogen, or oxygen,—was admitted at about atmospheric pressure, after which the cell was sealed and irradiated. Absorption curves of oil irradiated in this manner are shown in figure 3. An absorption curve of oil irradiated in this manner, but contained in an evacuated cell, is identical with the central curve of this figure. The only gas to take part in the reaction is oxygen. It is interesting to note that there is no additional absorption

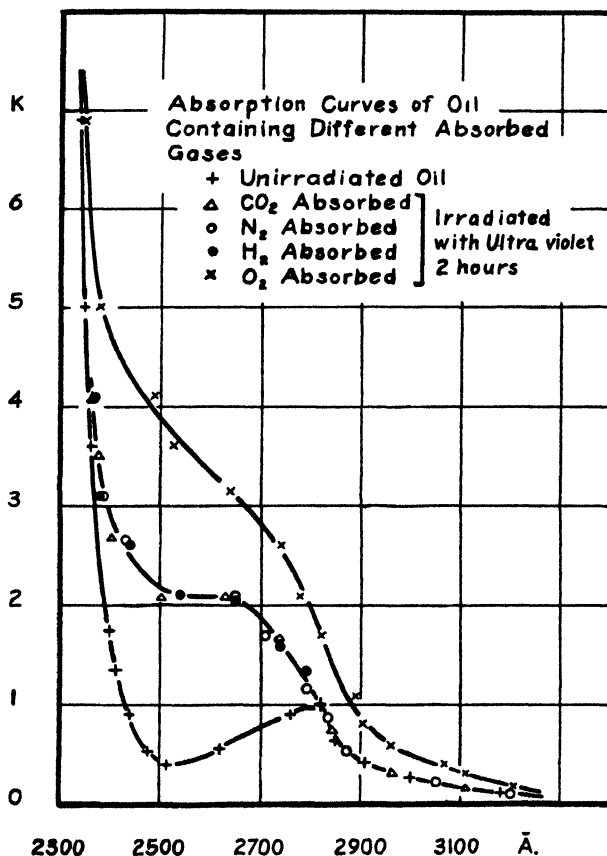


FIG. 3. Absorption curves of oil containing different absorbed gases

due to the unoxidized products formed in wave lengths longer than 2900 Å., and that the difference in absorption between the unirradiated oil and the oil containing gases other than oxygen, which is probably due to unsaturated unoxidized hydrocarbon molecules, reaches a maximum at about 2500 Å. The additional absorption due to the oxidized oil has no definite long wave length limit where the absorption becomes negligibly small. There is little significant difference, as indicated by the absorption

curves, between the products formed by x-ray or ultraviolet irradiation (figures 1 and 2), if curves of equivalent exposure are compared. The slightly steeper slope at 2800 Å. for the x-ray irradiated oil might indicate a relatively greater absorption due to unsaturated molecules in the case of the x-rays than with ultraviolet irradiation.

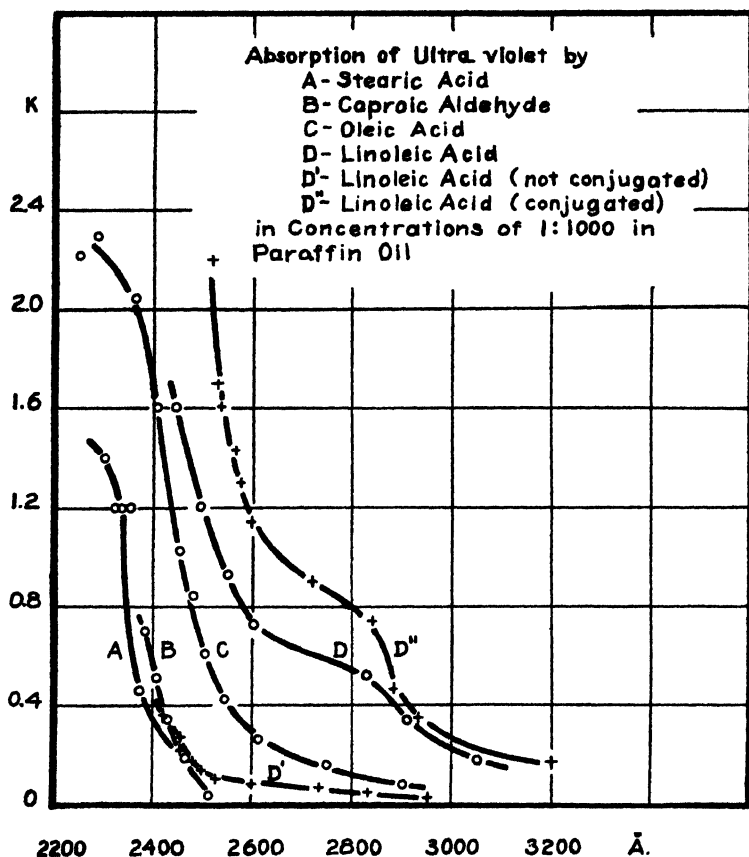


FIG. 4. Absorption of ultraviolet light by stearic acid, caproaldehyde, oleic acid, and linoleic acid.

Possible types of molecules that can result from irradiations of these sorts are extremely numerous. Mass spectrographic data obtained by Baker and Tate (2) show all possible disintegration forms of isobutane and *n*-butane, when the molecules are bombarded with electrons of about 80 electron-volts energy. The products were observed as singly charged ions. All degrees of unsaturation were found. As a gas under very low pressure was considered, only disintegration products were observed. In a liquid when a long straight-chain hydrocarbon is ionized, it may dis-

sociate, giving rise to a variety of lighter saturated and unsaturated hydrocarbons and hydrogen (4, 5), or it may, under suitable conditions, polymerize with certain hydrocarbons. Stoppered test-tubes containing oil and irradiated with x-rays developed an explosive gas in the space above the oil. Other experiments (4, 5) led us to believe this gas to be mostly hydrogen, methane, and other saturated hydrocarbons.

In figure 4 is given the absorption due to caproaldehyde, stearic acid, oleic acid, and different forms of linoleic acid,² when these substances are dissolved in small proportions in oil. Curve D represents an old sample of linoleic acid of unknown isomeric content. In the determination of these curves the pure oil was used in the comparison cell; hence the absorption given is due only to the material added to the oil. Figure 5 shows the additional absorption of oil caused by irradiation. These curves are derived from figure 2. As the values of the extinction coefficient below 2400 Å. represent differences between large, rapidly varying quantities, they cannot be considered very accurate. The absorption curves of figure 4 show, as is expected, that the absorption becomes greater and extends further toward the visible as the degree of unsaturation is increased. Substances like caprylene and cetyl alcohol give very little absorption. According to some very recent work of Burr, Miller, and collaborators (3) the proximity of a pair of double bonds to one another makes an enormous difference in the absorption coefficient. Thus it would be possible to obtain linoleic acid in two isomeric forms whose absorption coefficients might vary a hundredfold at a given wave length. The conjugated form has the greatest absorption.

These data indicate that the oxidation products formed by irradiation and illustrated in the absorption curves are oxidation products formed from materials of a high degree of unsaturation, for saturated acids, alcohols, and aldehydes, and carbohydrates containing a single double bond would not be noticed in the absorption curves of the irradiated oils, as their absorption is too small above 2600 Å. Oxidation products containing two or more double bonds, probably conjugated, appear to be necessary in order that the large amount of absorption at 2700 Å. be present with the small quantities of materials formed. The dissimilarity of the curves of the two figures (figures 4 and 5) suggests that the fatty acid component is not a predominant part.

Polyethylenic molecules with unconjugated double bonds can be reduced to the conjugated form by a prolonged treatment with a solution of alcoholic potassium hydroxide (3, 8). Twenty-five milliliters of the oil to be tested, 25 ml. of a solution of 25 g. of potassium hydroxide plus

² The authors wish to express their appreciation to Drs. Burr, Miller, and Kass of the Botany Department of the University of Minnesota for the linoleic acids used in these experiments.

25 ml. of water, and 200 ml. of 95 per cent ethyl alcohol were placed in an all-Pyrex refluxing apparatus. The mixture was boiled for 24 hr. Oil from the mixture was removed from the other components and washed with water in a separatory funnel. The emulsion was removed from the oil by filtration through filter paper.

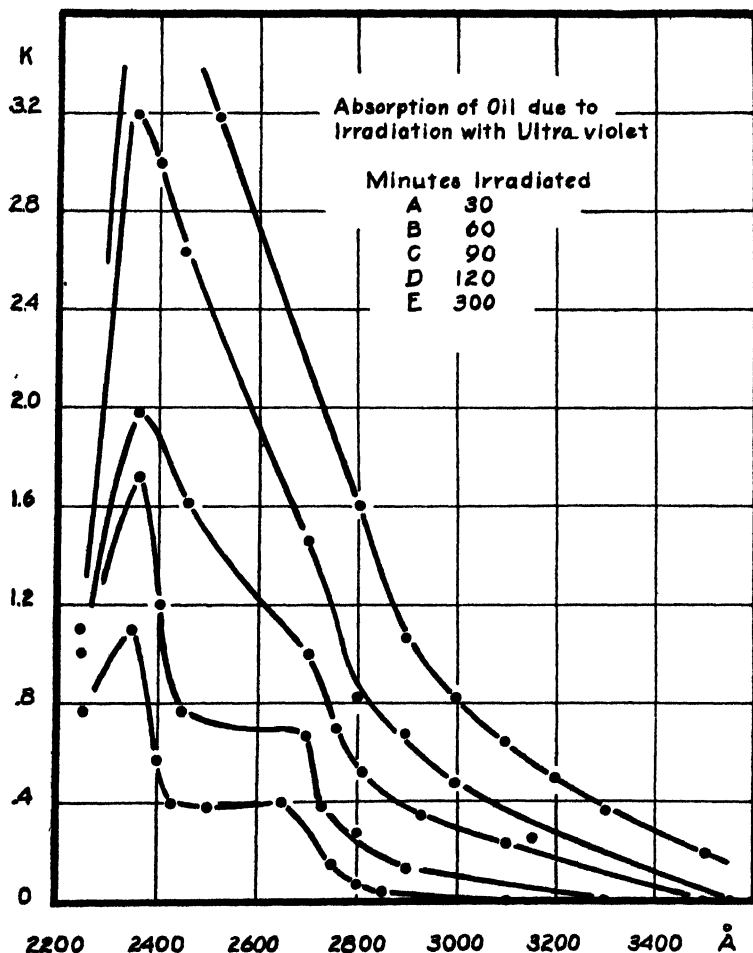


FIG. 5. The additional absorption of oil, due to irradiation with ultraviolet. The absorption due to the unirradiated oil has been subtracted from these curves.

Three samples of oil that had been irradiated 1 hr. with ultraviolet light were taken. The first sample was refluxed 24 hr. in the alcoholic potassium hydroxide mixture and washed with water; the second sample was mixed with alcohol and washed with water; the third was not treated. The difference in the extinction coefficient for the three samples after the

above treatments was less than 0.1 down to 2330 Å., which is less than 3 per cent variation at 2330 Å. and less than 8 per cent at 2700 Å. Oil taken from the refluxed first sample would not spread on alkaline water; that from the washed second sample would spread to about half the area of the untreated third sample. Therefore some hydrophilic molecules must have been removed by the treatment of the first two samples.

It may be concluded from these results that the quantity of hydrophilic molecules is too small to cause appreciable absorption, and that the poly-ethylenic molecules formed are predominantly conjugated.

BEHAVIOR OF OIL DROPS ON WATER

If test tubes are half filled with oil, stoppered, and irradiated with x-rays, the maximum areas to which the drops (8.7 mg. each) of oil taken from these test tubes will spread when placed on slightly alkaline water are shown in figures 6 and 7. The amount of hydrophilic molecules formed is a function only of the x-ray dose, and, within reasonable limits, is independent of the hardness and intensity of the x-ray beam. The very different spreading properties of oil drops containing small amounts of dissolved stearic acid, and oil drops from irradiated oil, is illustrated in figure 7. Drops of oil containing small amounts of unsaturated fatty acids will, when placed on slightly alkaline water, contract very little from their maximum area. They behave more like drops of irradiated oil. It is interesting to note that the minimum x-ray dose required to give an appreciable spreading of an oil drop on water is about 15 kiloroentgens, which is about one-fourth the dose required to give a measurable change in absorption.

It is probable that it is necessary for the active end of the hydrophilic molecule to ionize, when in contact with the water, in order that the attraction be great enough to hold it at the interface. This is not true for monomolecular films. Cetyl alcohol, caproaldehyde, or caprylene do not cause spreading of oil drops on alkaline solutions; however, the last two are of such short chain length that they may be slightly soluble in the water. Adam (1b) states that if the chain has twelve carbon atoms or less, a monomolecular film made from the molecules may dissolve in the solution. However, the attraction of the oil at one side of an interface film should make the film less likely to dissolve in the water.

It is believed that the acid component of the oil gathered at the water-oil interface causes the drop to spread on an alkaline water solution. If the area over which the drop spreads is very large, this area is approximately proportional to the concentration of the acid in the oil. Information as to the degree of unsaturation of the acids can be obtained by noticing how the oil containing these acids spreads over water containing different substances in solution.

The spreading properties of oil containing small concentrations of stearic, oleic, or linoleic acid have been studied and compared with the spreading properties of irradiated oil. These spreading properties have been observed on alkaline and acid water, and on alkaline water containing calcium ions. Stearic, oleic, and linoleic acids possess, respectively, zero, one, and two double bonds. Two kinds of linoleic acid were used, the conjugated 9,11 linoleic acid and the unconjugated acid. Oil drops of the same volume and containing the same concentration of these materials will spread to approximately the same area on 0.01 normal sodium hydroxide. However, the oil containing the stearic acid contracts quite rapidly from the maximum area (figure 7) while the others do not. If

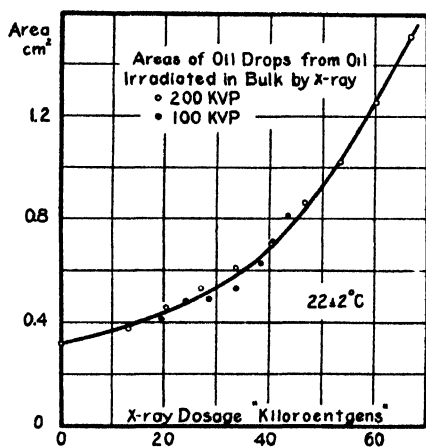


FIG. 6

FIG. 6. Maximum area attained by oil drops placed on 0.01 normal solution of sodium hydroxide. (Oil drops from a calibrated tungsten wire weigh 8.7 mg.)

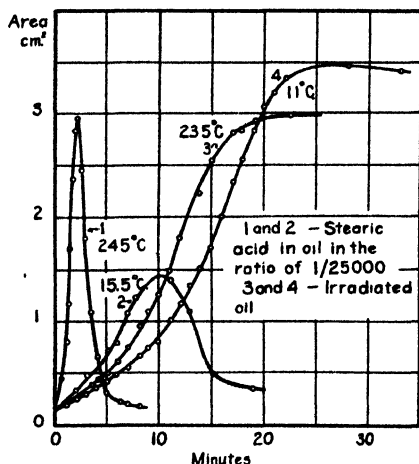


FIG. 7

FIG. 7. Spreading of oil drops on 0.01 normal sodium hydroxide

calcium chloride is dissolved in the 0.01 normal sodium hydroxide, the oil drop containing the stearic acid will not spread, although the drops containing the oleic and linoleic acids spread as before. When a drop of oil containing stearic acid in relatively large concentrations, as 1:1000, is placed on the calcium salt solution, a thick jagged film is seen to emerge from the interface. Evidently the calcium combines with the stearate ion as soon as diffusion brings them together, the resulting calcium stearate forming a solid film many molecules thick. If 0.01 normal hydrochloric acid solution is used in place of the alkaline solution, oil containing 9,11 linoleic acid in high concentration spreads slowly to form an unstable film. Oil drops containing stearic, oleic, or unconjugated linoleic acids do not spread. Oil drops from irradiated oil spread similarly to con-

jugated linoleic acid in all of these cases, with the exception that the film formed by the irradiated oil on acid water is quite stable.

When both stearic and linoleic acid are dissolved in oil, the area attained by an oil drop on 0.01 normal sodium hydroxide is equivalent to that expected from the sum of the concentrations. The area attained by an oil drop from this mixture, when the oil drop was placed on alkaline

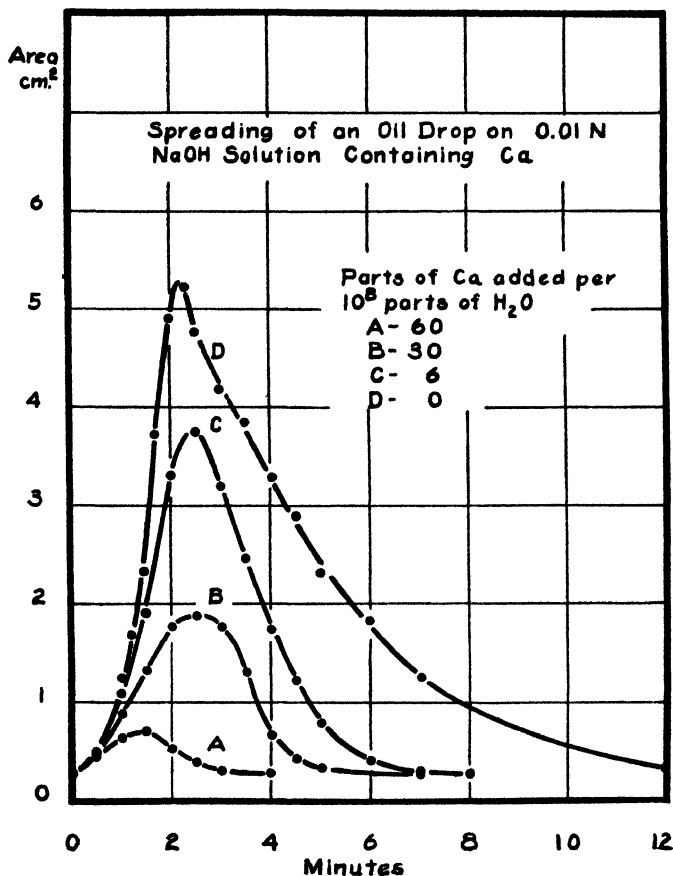


FIG. 8. Spreading of oil drops containing stearic acid in a concentration of 1:20,000 by weight.

water containing calcium, corresponds to the linoleic acid concentration. The areas attained by the irradiated oil were the same in either solution.

It is concluded that the acids and probably the oxidized molecules formed are almost all unsaturated. It is likely that the oxidation is due to more highly reactive unsaturated hydrocarbons, which are formed first by irradiation and later, under suitable stimuli, react with the oxygen.

Figure 8 illustrates the spreading of oil drops (8.7 mg.), containing stearic acid in concentrations of 1:20000 by weight, on 0.01 normal sodium hydroxide containing known amounts of calcium ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$). Different ions in solution exert very different effects upon the spreading properties of oil drops containing the hydrophilic molecules. With the areas being functions of the temperature, the hydrogen-ion concentration of the water, the time, the concentration, and the kind of hydrophilic molecule in the oil, it is possible that tests involving these conditions may be used in the chemical analysis of minute concentrations of certain ions.

DETERMINATION OF UNSATURATION AND ACIDITY BY CHEMICAL METHODS

Chemical tests of the type necessary to determine the acid and iodine numbers are not accurate, owing to the small quantities of materials involved and the difficulty in determining the end point of the reactions colorimetrically. The values presented indicate mainly an order of magnitude rather than an exact quantitative determination. The acid test (the acid number is the number of milligrams of potassium hydroxide necessary to neutralize the acids in 1 g. of oil) results in zero acid number for unirradiated oil, while for oil irradiated with ultraviolet for 5 hr. the value 0.03 is obtained. If the average molecular weight of the acid molecule is taken as 200, then the number of milligrams of acid per gram of oil would be 0.12 and the number of acid molecules per drop of oil (8.7 mg.) is about 3.2×10^{16} . Langmuir (7b) gives the area per stearic acid molecule in contact with the oil at the interface of an oil-water film as $88 \times 10^{-16} \text{ cm.}^2$; experiments carried out in this laboratory approximately verify this value for oil drops if the interface area is large. The area of the oil drop in the above case, as calculated from the acid number, should be about 28 cm.^2 , which is about half the observed value. Absorption due to possible oxidation products, estimated from figures 3 and 4, roughly indicates a concentration of 1:1000 for these products in the oil, for oil containing oxygen and irradiated 2 hr. with ultraviolet light. This is a concentration about ten times greater than that of the substance causing the oil drops to spread after the oil was irradiated 5 hr. The absorption of these products is assumed to be comparable to that of conjugated linoleic acid. It has been shown that the acid molecules formed exhibit properties of the more unsaturated types. From these considerations it is indicated that the spreading of the oil drop is caused mainly by the acid, and not by other oxidized or unsaturated hydrocarbons. Drops from oil irradiated in a vacuum do not spread on a water surface.

The iodine number is equal to the number of grams of iodine that 100 g. of oil is capable of absorbing. Normally it is a test for the relative degree of unsaturation in fats. It is realized that the values obtained cannot be strictly interpreted as a measure of unsaturation, for it is not

certain how near to completion the reaction is carried, nor is it known how the iodine, or its equivalent in bromine, will react with the materials in the oil. If it is assumed that for each two of the iodine atoms absorbed we have a double bond, and if it is further assumed that there is but one double bond per molecule, then with a molecular weight of 200 the following concentrations result from oil irradiated in the open culture dishes by ultraviolet light:

IRRADIATION TIME	IODINE VALUE	PER CENT CONCENTRATION
<i>hours</i>		
0	0.03	0.04
1	0.18	0.23
5	0.25	0.32
27	0.29	0.37

The per cent concentration is not of great significance for the type of molecule for which the table was calculated, as it appears that many of the unsaturated molecules are more complicated than those with but one double bond. The per cent concentration is of the order of a few tenths of 1 per cent, which would be as indicated by the absorption data for molecules with conjugated double bonds. The fact that the iodine value is not greater indicates that the materials formed that are not noticed in the absorption spectra cannot be present in predominantly large quantities. The small increase of the iodine number after several hours of irradiation of the oil makes it probable that polymerization begins to take place as soon as an appreciable number of unsaturated molecules are formed. This would also account for the saturation of absorbing materials formed, due to long irradiation of the oil with ultraviolet.

CONCLUSION

From all of the tests used it can be concluded that roentgen or ultraviolet radiation affects straight-chain saturated hydrocarbons in an evacuated container as follows: Unsaturation is produced in a small fraction of the molecules. Multiple or at least double unsaturation occurs in a considerable proportion of the unsaturated molecules. The conjugated isomers are formed to a great extent, if not to the complete exclusion of the other forms. An explosive gas, probably consisting of hydrogen and short-chain hydrocarbons, is also formed. Polymerization takes place after appreciable amounts of unsaturated materials are formed.

If the irradiation takes place in the presence of air (oxygen) a certain amount of oxidation is induced. Unsaturated fatty acids are formed. These are at least doubly unsaturated and are conjugated. It has been estimated that 100 kiloroentgens of x-rays produce one part of acid mole-

cules in 5×10^4 hydrocarbon molecules. At least ten times as many molecules are at the same time unsaturated without being oxidized to acids. The presence of such gases as hydrogen, nitrogen, and carbon dioxide during the irradiation does not seem to have any influence on the reaction.

Impurities in the water, especially calcium, cause large differences in the spreading of oil drops containing long straight-chain fatty acids.

REFERENCES

- (1) ADAM, N. K.: (a) *The Physics and Chemistry of Surfaces*. Clarendon Press, Oxford (1930). (b) *Proc. Roy. Soc. (London)* **A155**, 690 (1936).
- (2) BAKER, R. F., AND TATE, J. T.: *Abstract, Phys. Rev.* **53**, 944 (1938). Complete data will be published in the *Physical Review*.
- (3) BURR, GEORGE: Data not yet published.
- (4) EGLOFF, GUSTAV: *The Reactions of Pure Hydrocarbons*, American Chemical Society Monograph No. 73. Reinhold Publishing Corporation, New York (1937).
- (5) ELLIS, CARLETON: *The Chemistry of Petroleum Derivatives* (especially p. 274). The Chemical Catalog Co., Inc., New York (1934).
- (6) FRICKE, HUGO: *Cold Spring Harbor Symposia Quant. Biol.* **3**, 55 (1935).
- (7) LANGMUIR, I.: *Science* **84**, 379 (1936); *J. Chem. Phys.* **1**, 756 (1933); *J. Franklin Inst.* **218**, 143 (1934).
- (8) MOORE, THOMAS: *Biochem. J.* **31**, 138 (1937).
- (9) STENSTROM, W., AND VIGNESS, I.: (a) *J. Chem. Phys.* **5**, 298 (1937); (b) *Am. J. Roentgenology Radium Therapy* **40**, 427 (1938).

NEW BOOKS

Chemische Gasreaktion. By H. J. SCHUMACHER. 23 x 15 cm.; 487 pp. Dresden and Leipzig: Theodor Steinkopff, 1938. Price: unbound, 33.75 RM; bound, 35.25 RM.

This book is Volume III of the series *Die Chemische Reaktion* and deals with the kinetics and mechanism of homogeneous thermal reaction in gases.

During the last few years there have been many major developments in the theory of chemical change and at the same time an increased output of experimental material. Progress has been rapid, and there is no doubt that many of the fundamental principles governing the mechanism of simple chemical reaction are fairly soundly established. Although we must expect some modification and extension of the theory in the near future, the present is a very opportune time in which to review the position, and Professor Schumacher's book, in which he gives a thorough and completely modern account of these developments, is therefore very welcome.

The subject matter is excellently arranged, the book being divided into two sections,—theoretical and experimental,—the latter occupying about three quarters of the book. The theoretical treatment is based on the methods of statistical mechanics, and a detailed account of the use of quantum-mechanical methods for calculating activation energies and the absolute rates of simple chemical reactions is given.

The experimental results are treated under two general headings; the first covers simple reactions, the sections being subdivided into the general type of reaction involved (unimolecular, etc.), and the second covers chain reactions. It appears to the reviewer that all the experimental data of any importance on simple reactions, available up to the beginning of 1938, have been included: the sections on chain reactions are not so complete, since with the exception of the hydrogen-oxygen reaction little mention is made of the numerous oxidation reactions characterized by explosion limits. These omissions, however, are not important, since this type of reaction has been adequately dealt with recently in other volumes. As a whole, the second part of the book is complete in itself, and is suitable for those more interested in the experimental aspects than in the theory.

Excellent tables of useful data, such as physical constants, atomic and molecular diameters, and bond energies, are included. The book can be recommended to all interested in the mechanism of chemical reactions.

C. E. H. BAWN.

Kurzes Lehrbuch der physikalischen Chemie. Heft I. By KARL JELLINEK. 25 x 16 cm.; xi + 314 pp. Deventer: N. V. Uitgevers-Maatschappij A. E. Kluwer, 1938. Price: Fl. 8.50.

This is Part I of a one-volume textbook of physical chemistry, which is to be published in four parts. When completed the volume will be a shorter but still comprehensive account of the subject on the basis of the author's well-known five-volume textbook.

This part deals mainly with the elements of thermodynamics (very carefully developed), the elements of the kinetic theory of gases, and the laws of pure substances, of dilute gas mixtures, of dilute solutions of non-electrolytes, and of concentrated mixtures of non-electrolytes.

Teachers of physical chemistry will welcome the considerable emphasis that is laid by the author on the importance of numerical examples. A large number of these, many of which are not found in the usual books on calculations, are worked out. The elements only of the calculus are assumed, any more advanced mathematics being developed as and wherever required by the student.

The usual applications of the fundamental laws are made very interesting, since they are dealt with from the standpoints of (a) experimental work, (b) thermodynamics, (c) kinetics. In a book of this size the treatment of the experimental sections is not as extensive as is usual in the more elementary textbooks of physical chemistry in use in most of the chemistry schools in Great Britain, which are supplemented later in the course by the excellent range of monographs now at our disposal, but it can certainly be said that a young chemist brought up on a textbook of the type under review, if supplemented by a modern course of practical physical chemistry, should find himself admirably equipped in this branch of the subject.

D. C. JONES.

Sampling and Analysis of Carbon and Alloy Steels. Methods of the Chemists of the Subsidiary Companies of the United States Steel Corporation as revised to 1937. 356 pp. New York: Reinhold Publishing Corporation, 1938. Price: \$4.50.

This book replaces two former booklets dealing with the sampling and analysis of plain carbon steels and of alloy steels. Complete directions are given for sampling and for the qualitative identification of various types of steel, while the bulk of the book is devoted to methods of analysis of the various constituents of steel, including rare elements, such as zirconium, columbium, and tantalum. The number of literature references is very limited. The extensive table of contents at the beginning of the book takes the place of an index. The members of the committee who have coöperated in the publication of this text deserve great praise for having made available to analytical chemists these standard methods, which have been selected on the basis of the rich experience of, and much original research by, the authors. The book constitutes a tribute to the excellence of the analytical work that is being done by the chemists of the United States Steel Corporation.

I. M. KOLTHOFF.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 39: Seltene Erden. Lieferung 1. 26 x 18 cm.; pp. iii + 122. Berlin: Verlag Chemie, 1938. Price: 14.25 RM.

The present section is of particular interest, since it begins the volume of the *Handbuch* dealing with the rare-earth elements, which promises to be of great value and is eagerly awaited. This section deals with the history and occurrence of the elements. The historical section can only be described as a masterpiece of work in this field. It brings the story of investigations of the rare earths up to the modern period and makes use of an astonishing bulk of literature, including such important sources as the letters of Berzelius, in a most systematic and interesting manner. Those interested in the history of chemistry will find this section of absorbing interest, as it surveys a great field of difficult and fundamental experimental work. The elements are divided broadly into (1) scandium and yttrium, and (2) the lanthanides, the subdivisions of the latter being sensible and helpful. The symbol Tu is retained (instead of Tm) for thulium, and lutecium, according to general usage by German chemists, is called cassiopeium. The lanthanides are broadly divided into cerite earths and yttria earths (the latter being usually called gadolinite earths by English-speaking chemists). The section on the occurrence of the rare earths is very complete and the mineral sources are exhaustively considered, since this part

is of considerable economic interest; it is further enriched by a topographical survey, the earths found in various parts of the world being given under the place names. The sources of monazite are particularly well described. Out-of-the-way sources, such as plants, animals, and coal ash, are not forgotten. Altogether it may be said that if the remaining sections of the volume on the rare earths are as good as this one, chemists will have reason to be grateful to the patient, careful, and accurate work put in by the editor and his collaborators.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 25: Caesium mit einem Anhang über Ekacesium. Lieferung 2. 26 x 18 cm.; pp. xx + ix + 105-268. Berlin: Verlag Chemie, 1938. Price: 21.75 RM.

This section deals with the compounds of cesium and completes the volume on this element, the first part having dealt with the element. Compounds with hydrogen, oxygen, nitrogen, halogens, sulfur, selenium, tellurium, boron, carbon, silicon, phosphorus, arsenic, antimony, bismuth, and double salts with other alkali metals, and oxy compounds are fully dealt with. The order is that adopted in all volumes of Gmelin's *Handbuch* and goes back to the old issue, the periodic order not being followed. It goes without saying that all the information is complete, up-to-date, and critical. The literature on ekacesium is fully and critically reviewed and the conclusion is reached that "in the present stage of investigation, ekacesium either does not exist at all or exists only in extremely minute amounts."

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 27: Magnesium. Teil B. Lieferung 3. 26 x 18 cm.; pp. xiv + 331-422. Berlin: Verlag Chemie, 1938. Price: 12 RM.

This section includes cyanogen compounds, the formate, acetate, oxalate, tartrate, and compounds with silicon, phosphorus, arsenic, antimony, and bismuth. The organic acids are those chosen for inclusion in all parts of the *Handbuch* and represent those which form compounds of interest in inorganic chemistry. The information is very complete and critical on physical and physicochemical properties; numerical data, as well as the preparative and chemical properties and reactions, are given. The information is based on the latest literature, this being clear in the section on the phosphates, for example, and in some cases patent literature is reviewed; it is stated, for example, that magnesia is used in sugar refining. The section on silicates is very complete and well documented and is of considerable interest from the mineralogical side. The section is an excellent example of the high standard of the whole work.

J. R. PARTINGTON.

The Properties of Glass. By GEORGE W. MOREY. 561 pp. New York: Reinhold Publishing Corporation, 1938. Price: \$12.50.

This volume, which is an important contribution to the literature on glass, comes from the pen of one whose personal researches rank him as a leader in physicochemical development in the field of glass technology. It is natural, therefore, that he should stress the physical properties and testing of glass.

The introductory chapter on history and definition is unique, in that it includes archeological material as well as glass production. Chapter II, on devitrification, is a masterly presentation from the standpoint of the phase law, with which the

author has been greatly occupied. In chapter III, on composition, the section on volatile substances and their adsorption is timely, together with the permeability of glass to gases. Chapter IV, on chemical durability, discusses composition and testing, indicating discrepancies in the various methods employed for a given determination. Chapter V deals with the measurement of viscosity and theoretical considerations not only for glasses, but also for slags and minerals. Chapter VI, on annealing, discusses the detection and measurement of strain, the development of strains in glass, and methods for their removal. The annealing of common types and special glasses is included. In chapter VII, on surface tension, units are listed with experimental results of their application. Chapter VIII, on the heat capacity of glass, discusses single- and multi-component systems. Chapter IX covers thermal conductivity, providing mathematical formulae and data for individual glass-making oxides. Chapter X, on density, gives the individual values commonly employed in additive calculations and applies these to uni- and multi-component systems. Density is discussed not only at ordinary temperatures, but also for higher temperatures. In chapter XI thermal expansion, methods of measurement, and the effect of heat are treated. Chapter XII deals with elastic properties. Compressibility, and the effects of temperature, pressure, and strain on elastic constants, are followed by a discussion of the elastic after-effect. In chapter XIII, on the strength of glass, units and various component systems are given with a comparison of the strength of fibers and tubes. The effect of strain on strength, of duration of load during tests, and finally that of temperature on strength is indicated. In chapter XIV thermal endurance and optical differences with temperature changes are illustrated. In chapter XV, on hardness, the uncertainty and variation of values is indicated, and it is clear that this property cannot yet be satisfactorily determined by any standard method. Optical properties are discussed in chapter XVI. After defining the units, the author lists experimental methods for determination of refractive index and dispersion. Valuable data are provided for a great variety of glasses. Finally, the effect of pressure on optical properties is covered, with units and experimental data given, and a short section covers transmission values for colored glasses. This is one of many valuable chapters in the book. In chapter XVII the electrical conductivity of glass, which was covered more extensively in the "Electrical Properties of Glass" with J. T. Littleton in an earlier publication, is given generous treatment. Chapter XVIII, on dielectric properties, treats the effects of frequency, temperature, chemical composition, surrounding media, and applied voltages, and discusses the nature of dielectric failure. Variations with thickness are also covered. Chapter XIX, on magnetic properties, deals with the Faraday and Kerr effects. The last chapter, chapter XX, on the constitution of glass, stresses the importance of x-ray analysis, variations of this with temperature, and changes on annealing. The difference in the appearance of pure crystals and glasses is illustrated and emphasized.

Not all technologists will agree with the author concerning methods to which he has given preference. The applicability of a particular method for a special case may vary with the type of glass. Very frequent reference to the author's publications clearly indicates the extent of his own contributions. In the index errors occur occasionally, but there is an abundance of cross reference information. A supplementary index on the properties of glasses in various systems is an aid rarely encountered in publications. Dr. Morey's volume is a precious addition to the literature on glass.

ALEXANDER SILVERMAN.

THE RELATIONSHIP BETWEEN THE VISCOSITY OF A LIQUID AND THE VAPOR CONCENTRATION

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Further knowledge of the relationships between and among various physical and chemical properties of pure liquids and solutions is needed for a better understanding of the liquid state. Certain of these properties, for example, fluidity and vapor pressure, are only indirectly related to each other, because they are in turn dependent upon some other property.

In 1868 Rellstab (6) compared the viscosities of various liquids at temperatures at which the vapor pressures were the same and also at a given temperature, but found no simple quantitative expression for his data. Later Porter (5) pointed out that in general, when comparison is made at ordinary temperatures, liquids which are quite viscous have relatively low vapor pressures, whereas those which are quite fluent have relatively high ones. Bingham (2) has shown that if the fluidities of certain aliphatic ethers are plotted against their corresponding vapor pressures, the points fall on or near a single curve. For a number of substances he plotted the reduced fluidities, which were calculated by using the fluidity of heptane at the boiling point as a standard, against the corresponding vapor pressures and obtained curves which were quite similar.

An expression connecting the fluidity and the corresponding vapor pressure of a pure liquid can readily be deduced from a theoretical foundation. The equation

$$\eta = \alpha T^{-\beta} e^{(\gamma/T + \delta T)} \quad (1)$$

in which η is the absolute viscosity, T is the absolute temperature, e is the base of the natural system of logarithms, and α , β , γ , and δ are constants, has been derived from a thermodynamic and kinetic basis (1).

In the integrated form the Clausius-Clapeyron equation is

$$\ln P = -\frac{\Delta H}{RT} + K \quad (2)$$

Combining this with equation 1

$$P = R\eta^{\kappa_1} T e^{(\kappa_2/T - \kappa_3 T + \kappa_4)} \quad (3)$$

where $K_1 \dots K_4$ are constants.

Since $P = CRT$, the Clausius-Clapeyron equation can be written as

$$\ln C = -A/T - \ln T + B \quad (4)$$

where $A = \Delta H/R$, $B = K - \ln R$, and C is the concentration of the vapor in moles per liter. Combining equations 1 and 4

$$\varphi C^\beta = e^{(K''/T - \beta T + K')} \quad (5)$$

where $-\beta A - \gamma = K''$, $-\ln K + B\beta = K'$, and φ is the fluidity of the liquid.

Obviously

$$C = \eta^{K_1} e^{(K_2/T - K_3T + K_4)} \quad (6)$$

Equations 3, 5, and 6 define both the liquid and its saturated vapor.

EMPIRICAL FORMULAE

Since the above expressions are rather cumbersome for ordinary purposes of calculation, the writer has sought and found simpler relationships which are quite satisfactory for general usage.

When the logarithm of the fluidity in rhes of a large number of liquids is plotted against the logarithm of the corresponding vapor concentration in moles per liter, calculated from the gas law $C = P/RT$, in which P is the vapor pressure, curves result which, in general, are straight lines over wide temperature ranges. The equation for such curves is

$$\varphi = \varphi_0 C^m \quad (7)$$

φ_0 and m are constants characteristic of a given liquid. The former will be termed the "reference fluidity" and is, theoretically, the fluidity when the concentration in the vapor phase is 1 mole per liter. It is noted that

$$m = \frac{d \ln \varphi}{d \ln C} = \frac{\ln \varphi / \varphi_0}{\ln C} \quad (8)$$

The linearity of the curves for certain substances is shown in figure 1. In table 1 are given values of the constants m and φ_0 for fifty-two pure liquids. Vapor pressure data in millimeters of mercury and absolute viscosities in poises were obtained from the International Critical Tables and the Landolt-Börnstein Tabellen. In general, the procedure used was to read the viscosities from a viscosity *versus* temperature curve of a given liquid for those temperatures at which vapor pressures were actually given in the afore-mentioned tables. After making calculations for fluidities and vapor concentrations, the best possible straight line was drawn through the log-log plot and the values of φ_0 and m calculated from data read from the curve. The method of least squares was not used in

deducing the constants, as the above procedure was considered sufficiently accurate.

By means of the above empirical equation fluidities can be calculated which agree with experimental values with an accuracy, in general, of within about ± 2 per cent for the liquids listed and over the temperature ranges given. Many of the available vapor pressure data are inaccurate.

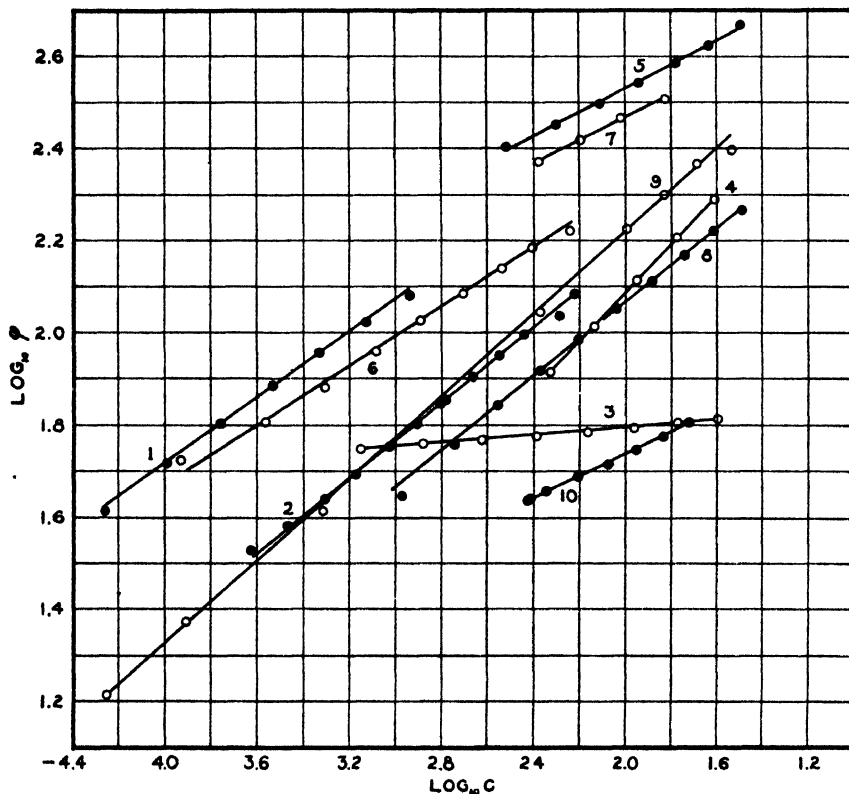


FIG. 1. Curves for a number of liquids showing the linear relationship between the logarithm of the fluidity, ϕ , in rhes and the logarithm of the vapor concentration, C , in moles per liter. Curves: 1, *o*-toluidine; 2, *n*-butyl alcohol; 3, ethyl alcohol; 4, isobutyl alcohol; 5, ethyl propyl ether; 6, aniline; 7, methyl ethyl ketone; 8, formic acid; 9, isoamyl alcohol; 10, iodine.

Whether the relationship applies over wider temperature ranges than those given can only be determined when further overlapping values for viscosities and vapor pressures are available.

Deviations of certain of the curves from straight lines occur at lower temperatures and are, perhaps, due to association. Water, which shows an anomalous behavior in so many properties, likewise does so in this case. It would be of interest to compare the log fluidity-log vapor concentration

TABLE 1

Values for certain pure liquids of the constants φ_0 and m in the expression $\varphi = \varphi_0 C^m$

LIQUID	TEMPERATURE RANGE	m	φ_0
	°C.		
Chlorine	(-80) - (-40)	0.192	366
Bromine	(-7.3) - 35	0.255	328
Iodine	114 - 170	0.241	167
Sulfur	120 - 150	0.310	536
Mercury	0 - 340	0.046	136
Water*	40 - 100	0.325	1070
Carbon dioxide	5 - 29	0.545	645
Carbon disulfide	0 - 50	0.208	398
Hexane	0 - 70	0.232	996
Heptane	0 - 100	0.228	1003
Octane	0 - 130	0.237	1079
Isopentane	(-30) - 50	0.272	1130
Diisopropyl	0 - 30	0.304	1046
Benzene	7.8 - 90	0.319	930
Toluene	0 - 110	0.291	1100
Ethylbenzene	0 - 130	0.289	1146
<i>o</i> -Xylene†	20 - 140	0.287	1112
<i>m</i> -Xylene	10 - 140	0.228	1000
<i>p</i> -Xylene‡	30 - 140	0.292	1264
Cyclohexane	20 - 40	0.434	1108
Methylene chloride	0 - 30	0.271	675
Chloroform	(-10) - 61	0.255	598
Carbon tetrachloride	0 - 100	0.352	664
1,1-Dichloroethane	7 - 55	0.280	745
1,2-Dichloroethane	0 - 81	0.304	680
1,1,2,2-Tetrachloroethane	25 - 80	0.326	779
Tetrachloroethylene	40 - 110	0.234	576
Trichloroethylene	25 - 80	0.215	599
Methyl iodide	0 - 30	0.255	572
Ethyl iodide	0 - 60	0.241	593
Iodobenzene	5 - 150	0.237	661
Methyl sulfide	0 - 40	0.235	832
Methyl alcohol	0 - 60	0.296	803
Ethyl alcohol	0 - 70	0.038	73 6
Propyl alcohol	0 - 100	0.421	896
<i>n</i> -Butyl alcohol	20 - 75	0.330	615
Isobutyl alcohol	60 - 100	0.530	1388
Isoamyl alcohol	10 - 130	0.444	1261
Ethyl ether	(-100) - 50	0.230	999
Methyl propyl ether	0 - 35	0.255	1078
Ethyl propyl ether	0 - 60	0.259	1111

* Does not fit below 40°C.

† Does not fit below 20°C.

‡ Does not fit below 30°C.

TABLE 1—*Concluded*

LIQUID	TEMPERATURE RANGE °C.	m	φ_0
Acetone	(-90) - 56.3	0.223	873
Methyl ethyl ketone	20 - 50	0.268	1017
Formic acid	10 - 100	0.401	736
Acetic acid	20 - 100	0.295	1425
Propionic acid	20 - 140	0.235	696
Butyric acid	20 - 155	0.248	766
Valeric acid	60 - 100	0.186	502
Isobutyric acid	30 - 155	0.244	759
Aniline	50 - 144	0.329	947
<i>o</i> -Toluidine	40 - 100	0.361	1427
<i>p</i> -Toluidine§	80 - 180	0.253	712

§ Does not fit below 80°C.

curve for deuterium oxide with that of ordinary water, since it seems that the former is less associated (3). However, available data for both vapor pressures and viscosities of heavy water do not overlap sufficiently in temperature range to make a fair test.

Molten sulfur exists in at least two modifications and the temperature-viscosity curve has a maximum, whereas the vapor pressure rises continuously with temperature increase. The log-log curve is shown in figure 2, but the linear relationship holds only up to about 150°C.

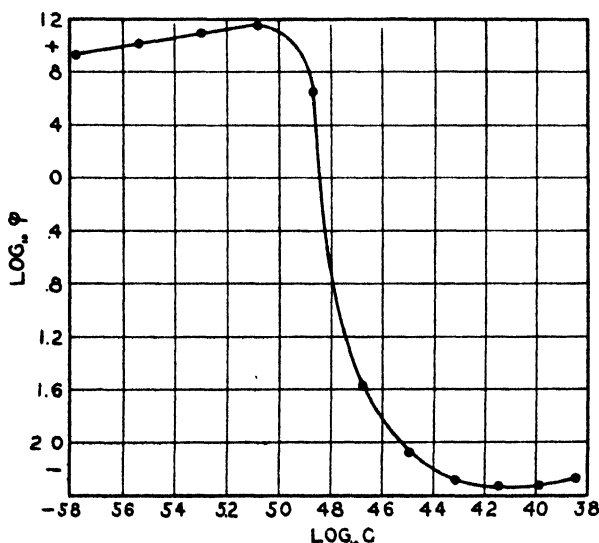


FIG. 2. Liquid sulfur. Plot of the logarithm of the fluidity, φ , in rhes versus the logarithm of the vapor concentration, C , in moles per liter.

The equation

$$\varphi = \varphi_0 C^m$$

can be written in the form

$$P = RT(\varphi/\varphi_0)^{1/m} \quad (9)$$

since $C = P/RT$. Unless we consider the possible existence of super-saturated or subsaturated vapors, there is only one independent variable in this expression, for fixing one determines the magnitude of the other two.

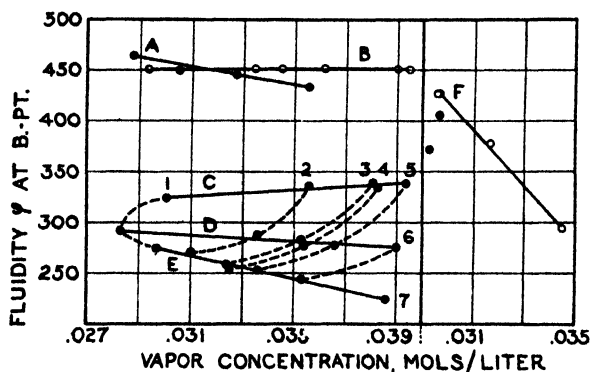


FIG. 3. Plot of the fluidity, φ , in rhes at the boiling point *versus* the vapor concentration, C , in moles per liter for a number of compounds. Points from left to right: Curve A, nonane, octane, heptane, and hexane; curve B, di-*n*-butyl, dipropyl, ethyl isobutyl, ethyl propyl, methyl propyl, and diethyl ethers. Curve F: open circles, *p*-xylene, *m*-xylene, toluene, and benzene; closed circles, *o*-xylene and ethylbenzene. Curves C, D, and E: chlorides, bromides, and iodides, respectively; dotted curves, 1 to 6 inclusive, phenyl, isobutyl, propyl, allyl, isopropyl, and ethyl, respectively. Point at 7, methyl iodide.

Assume, for a given liquid, that conditions are such that a supersaturated vapor exists, then

$$\left(\frac{\partial \varphi}{\partial P}\right)_T = \mu P^{m-1} \quad (10)$$

where μ is equal to $m\varphi_0/RT$. Next consider, theoretically, such conditions that the vapor pressure does not change with change in temperature, then

$$\left(\frac{\partial \varphi}{\partial T}\right)_P = -\chi T^{-m-1} \quad (11)$$

where $\chi = m\varphi_0(P/R)^m$. Thus the total differential is

$$d\varphi = \mu P^{m-1} dP - \chi T^{-m-1} dT \quad (12)$$

Bingham (2) found that the curves connecting the plotted fluidities of certain aliphatic hydrocarbons, ethers, and halides at their boiling points are linear. In figure 3 are plotted data showing the linear relationship between vapor concentration and fluidity at the boiling point for certain organic halides, members of the homologous series C_nH_{2n+2} , aromatic hydrocarbons, and ethers. Although points for quite diverse chlorides, bromides, and iodides lie on or near their respective straight lines, the chloride, bromide, and iodide of any given radical do not. Fluidities at the boiling points were obtained by extrapolation of the fluidity-temperature curves.

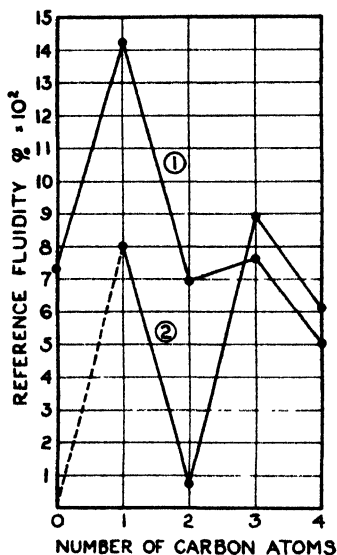


FIG. 4

FIG. 4. Curves showing the alternation in the reference fluidity, ϕ_0 , with odd and even number of carbon atoms. Curve 1, acids $C_nH_{2n+1}COOH$. Curve 2, alcohols $C_nH_{2n+1}OH$. The carbon atom of the carboxyl group of the acids has been excluded.

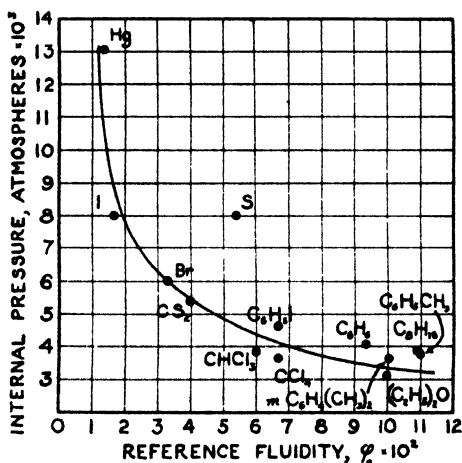


FIG. 5

FIG. 5. Variation of the internal pressure in atmospheres with the reference fluidity, ϕ_0 , for a number of liquids.

When the reference fluidities of alcohols and acids belonging to the homologous series $C_nH_{2n+1}OH$ and $C_nH_{2n+1}COOH$, for which data are available, are plotted against the number of carbon atoms present, alternations occur in the resulting curves (figure 4).

It is to be expected that in the case of two liquids, in one of which the attractive forces acting among the molecules are relatively greater than in the other (when comparison is made under like conditions), the fluidity of the latter liquid will be the greater. That such is the case is shown by the curve of figure 5, in which the internal pressures of a number of liquids

are plotted against the fluidities,¹ φ_0 . The internal pressures of liquids are not accurately known. Data used were those of Hildebrand (4).

VARIATION OF FLUIDITY WITH TEMPERATURE

Since

$$\frac{d \ln P}{dT} = \Delta H/RT^2$$

and

$$P = RT(\varphi/\varphi_0)^{1/m}$$

then

$$\frac{d \ln RT(\varphi/\varphi_0)^{1/m}}{dT} = \Delta H/RT^2 \quad (13)$$

and

$$\log \frac{\varphi_2}{\varphi_1} = m[0.0522\Delta H(1/T_1 - 1/T_2) - \log T_2/T_1] \quad (14)$$

Thus a semi-empirical expression showing the variation of fluidity with absolute temperature is obtained. A test of this equation is given in table 2. ΔH , in international joules per mole, has been calculated for ten

TABLE 2
Test of the application of equation 14 of text

LIQUID	φ_1	φ_2	P_1	P_2	T_1	T_2	ΔH (EQUA- TION 14)	ΔH (CLAU- SIUS- CLAPEY- RON EQUA- TION)	PER CENT DEVIATION FROM CLAU- SIUS- CLAPEY- RON RESULT
	<i>rhes</i>	<i>rhes</i>	<i>mm.</i>	<i>mm.</i>	$^{\circ}K.$	$^{\circ}K.$	<i>joules per mole</i>		<i>per cent</i>
Carbon disulfide.	291.5	333	432.7	854.0	303	323	29,230	27,680	+5.59
<i>p</i> -Xylene..	289.9	427.4	142.0	624.9	353	403	34,530	35,070	-1.54
<i>m</i> -Xylene...	142.3	401.6	3.45	448.9	283	393	41,060	40,950	+0.27
Benzene...	129.8	238.0	40	300	280.9	325.7	34,760	34,210	+1.64
Trichloro- ethylene...	190.5	260.4	94	453.0	303	343	34,110	34,000	+0.32
Aniline...	91.4	153.1	18.0	96.6	353	393	48,370	48,480	-0.23
Ethyl iodide	138.9	225.2	41.5	364.0	273	323	31,870	31,860	+0.03
Chlorine...	131.6	198.0	58.7	594	193	233	21,600	21,630	-0.14
<i>o</i> -Toluidine..	52.1	90.2	2.1	10.5	323	353	50,870	50,860	+0.02
Ethyl propyl ether	282.5	420.2	89.1	472.1	283	323	31,650	31,680	-0.09

¹ In making comparisons it would probably be better to reduce the vapor concentrations to standard conditions, and thus values of φ_0 would be given when the vapor concentration is 1 mole per liter under such conditions. However, this procedure changes φ_0 only slightly for ordinary liquids and for purposes of plotting is of no significance.

liquids chosen at random, using the above equation and the integrated form of the Clausius-Clapeyron equation. Column 10 shows the percentage deviations from the Clausius-Clapeyron results to be small.

For other equations expressing the variations of viscosity or fluidity with temperature, the reader is referred to Bingham (2) and to Souders (7).

It has been found that the relationship

$$\rho = D/T^m \quad (15)$$

where ρ is the density of the liquid and D is a constant characteristic of the liquid, approximately expresses the variation of density with absolute temperature. This equation utilizes the constant m defined by equation 8.

TABLE 3

Test of the application of the equation $(T_2/T_1)^m = \rho_1/\rho_2$

LIQUID	t_1	t_2	$(T_2/T_1)^m$	ρ_1/ρ_2	PER CENT DIFFER- ENCE
Carbon tetrachloride	0	40	1.0493	1.0498	-0.05
Chloroform	-10	55	1.0579	1.0870	-2.68
Formic acid	0	40	1.0563	1.0407	+1.54
Methyl iodide	0	30	1.0269	1.0363	-0.90
Ethyl iodide	0	60	1.0490	1.0749	-2.47
<i>n</i> -Propyl alcohol	0	100	1.1404	1.1194	+1.87
Methyl ethyl ketone.	20	50	1.0265	1.0409	-1.39
<i>n</i> -Butyric acid	25	80	1.0429	1.0607	-1.68
Iodobenzene	5	150	1.1046	1.1377	-2.91

A test of this relationship for a number of liquids is given in table 3. It has been applied in the form

$$\rho_1/\rho_2 = \left(\frac{T_2}{T_1}\right)^m$$

SOLUTIONS: LIQUID CONSTITUENTS ONLY

The fluidity, Φ , of an ideal solution consisting of two components is best given, according to Bingham (2), by the equation

$$\Phi = a_1\varphi_1 + a_2\varphi_2 - k(a_1 - w)(v_1 - v_2) \quad (16)$$

where a_1 = volume fraction of component A,

φ_1 = fluidity of pure component A,

v_1 = specific volume of A,

w = weight fraction of A, and

k = a constant.

Subscript 2 refers to component B.

For two or more components equation 16 can be written in the form

$$\Phi = a_1\varphi_1 + a_2\varphi_2 + \dots + a_n\varphi_n - f(\Delta v) \quad (17)$$

It is assumed, as by Bingham (2), "that if the volume is decreased for any reason by an amount Δv , the fluidity will be decreased by an amount which is some function of this, $f(\Delta v)$ ".

Since

$$\varphi_1 = \left(\frac{P_1}{RT}\right)^{m_1} \varphi_{01} \text{ etc.}$$

$$\Phi = a_1 \left(\frac{P_1}{RT}\right)^{m_1} \varphi_{01} + a_2 \left(\frac{P_2}{RT}\right)^{m_2} \varphi_{02} + \dots + a_n \left(\frac{P_n}{RT}\right)^{m_n} \varphi_{0n} - f(\Delta v) \quad (18)$$

Consider the case when Raoult's law holds, and when $m_1 = m_2 = \dots = m_n$, which may be true under ideal conditions and is approximately true for a number of liquids, as is shown in table 1.

$$p_1 = P_1 x_1, \text{ etc.}$$

Then

$$\Phi = \left(\frac{1}{RT}\right)^m \left[a_1 \varphi_{01} \left(\frac{p_1}{x_1}\right)^m + a_2 \varphi_{02} \left(\frac{p_2}{x_2}\right)^m + \dots + a_n \varphi_{0n} \left(\frac{p_n}{x_n}\right)^m \right] - f(\Delta v) \quad (19)$$

Hence

$$\Phi = \left(\frac{1}{T}\right)^m [k_1 a_1 P_1^m + k_2 a_2 P_2^m + \dots + k_n a_n P_n^m] - f(\Delta v) \quad (20)$$

When volume changes occur with temperature and are expressed as functions of the absolute temperature,

$$\Phi = k_1 f_1(T) P_1^m + k_2 f_2(T) P_2^m + \dots + k_n f_n(T) P_n^m - f(\Delta v) \quad (21)$$

TABLE 4

*Application of the equation $\varphi = \varphi_0 C^m$ to data concerning solutions of (a) benzene and carbon tetrachloride and (b) ethyl alcohol and water**

(a) BENZENE AND CARBON TETRACHLORIDE. TEMPERATURE RANGE 0-40°C.			(b) ETHYL ALCOHOL AND WATER. TEMPERATURE RANGE 20-75°C.		
Weight per cent benzene	m	φ_0	Weight per cent ethyl alcohol	m	φ_0
11.40	0.374	808	50	0.583	1272
22.37	0.376	867	60	0.561	1178
43.79	0.366	921	70	0.524	1047
67.03	0.352	935	80	0.486	962
			90	0.441	901

* For values of m and φ_0 for the pure components refer to table 1. C was calculated by using the sum of the vapor pressures of the two constituents.

The fluidity of the ideal solution is given in terms of the partial pressures of the constituents and the absolute temperature.

It is of interest to learn whether or not equation 7 is applicable to solutions consisting of liquid components. Mixtures of benzene and carbon tetrachloride are known to approach ideality (2). Equation 7 was found applicable to data covering a temperature range of 0° to 40°C. for these mixtures (table 4). However, in the case of mixtures of ethyl alcohol and water (20° to 75°C.) the equation does not fit when the weight per cent of alcohol is less than about 50 per cent. The curves are then similar to those for water, which is to be expected, as the mole fraction of water present is about 0.75 or higher.

SUMMARY

Empirical and theoretical expressions have been given showing the relationship between viscosity or fluidity and vapor pressure or vapor concentration. A semi-empirical equation has been deduced for the variation of fluidity with absolute temperature. Theoretical relationships have been given concerning the fluidity of solutions.

REFERENCES

- (1) ANDRADE: *Nature* **125**, 309 (1930).
 DRUCKER: *Z. physik. Chem.* **92**, 287 (1918).
 DUNN: *Trans. Faraday Soc.* **22**, 401 (1926).
 DE GUZMAN: *Anales soc. expañ. fís. quím.* **11**, 353 (1913).
 IYER: *Indian J. Phys.* **5**(14), 371 (1930).
 KENDALL AND MONROE: *J. Am. Chem. Soc.* **39**, 1799 (1917).
 LEDERER: *Kolloid-Beihefte* **34**, 270 (1931).
 MAXWELL: *Phil. Mag.* **35**, 129 (1868).
 RAMAN: *Nature* **111**, 532, 600 (1923).
 SHEPPARD: *Nature* **125**, 489 (1930).
- (2) BINGHAM: *Fluidity and Plasticity*, 1st edition. McGraw-Hill Book Co., Inc., New York (1922).
- (3) BINGHAM AND STEARNS: *J. Chem. Phys.* **2**, 107 (1934).
- (4) HILDEBRAND: *International Critical Tables*, Vol. IV, p. 19. McGraw-Hill Book Co., Inc., New York (1928).
- (5) PORTER: *Phil. Mag.* **23**, 458 (1912).
- (6) RELLSTAB: *Über die Transpiration homologer Flüssigkeiten*. Inaugural dissertation, Bonn, 1868.
- (7) SOUDERS: *J. Am. Chem. Soc.* **59**, 1252 (1937).

CHARACTERISTICS OF SILICATE PHOSPHORS

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Unlike the sulfide phosphors, which have been intensely studied by Lenard, the silicate phosphors have been rather neglected. Zinc silicate has been described by Lenard (8), and it and cadmium silicate have also been described by Uytterhoeven (12). They are similar to the sulfides, in that their fluorescence can be excited only in the presence of a foreign metal as activator at an optimum concentration. They differ from the sulfides, whose excitation is most strong under the near ultraviolet, by having their greatest excitation in the far ultraviolet in the neighborhood of the mercury line at 2537 Å. It is the aim of this paper to describe the effects of composition and treatment, the spectral characteristics of their fluorescence, and their responses to excitation by ultraviolet light.

Manganese is the strongest if not the only activator. It is added at an optimum concentration of about 0.5 per cent to a mixture of the constituent oxides. The phosphor is formed as a white powder by firing at an appropriate temperature.

I. SPEED OF REACTION

Because of its particularly high efficiency of light emission, zinc silicate was chosen for more detailed study. Some knowledge regarding the development of its fluorescence was secured by studies on the speed of reaction. That the speed of reaction in the solid state is dependent upon the rate of interdiffusion of the reacting constituents was demonstrated by Jander (7) for reactions of powdered magnesia and silica to form Mg_2SiO_4 . In the case of the phosphor the rate of diffusion was followed by heating a mixture of zinc oxide and silica with manganese oxide as activator, and by measuring the speed at which fluorescence developed with increase in time of firing. The velocity constant of the reaction was expressed as K in the equation

$$dF/dt = K(F_{\infty} - F)$$

where F_{∞} is the ultimate, saturated fluorescence, and F is the fluorescence measured at the time t in hours. The fluorescence was measured under excitation by light of wave length 2537 Å.

The phosphor was prepared in two ways: (a) from a mixture of powdered zinc and manganese oxides with silica, denominated a "powder mixture", and (b) from a solution of zinc and manganese nitrates in ethyl silicate. The latter was converted into a colloidal gel and then denitrated. It is known as a "gel mixture". The results are given in table 1. The velocity constant is shown to be five to six times greater for the gel than for the powder, a consequence of the greater fineness of division and intimacy of mixture.

The reaction is to be pictured as a diffusion of the constituent oxides through the shell of silicate that is formed around the reacting particles. This involves interchanges in position between neighboring atoms in the space lattice. The speed of the interdiffusion therefore depends upon the

TABLE 1

Speed of reaction for mixture of zinc oxide, silica, and 0.4 per cent manganese

TEMPERATURE	MIXTURE	K
°C.		
1250	Powder	1.40
1250	Gel	(ca.) 7.0
1000	Powder	0.17
1000	Gel	1.01
850	Powder	0.03
850	Gel	0.12

critical energy content of the atoms making these changes and can be expressed as

$$K = Ce^{-Q_D/RT}$$

where Q_D represents the heat of diffusion. A plot of the velocity constant K against $1/T$ is given in figure 1. From the slope the value of Q_D is calculated to be 20.4 Cal. for the phosphor prepared from powdered oxides, and 23.8 Cal. for that prepared from the gel. A value of about 40 Cal. was found by Jander for the diffusion of 1 mole of magnesium oxide into 10 moles of silica.

The rate of reaction was greatly increased by adding one of the non-volatile fluxes customarily used in the preparation of the sulfide phosphors. Its effectiveness lay in its ability to dissolve away the barrier of silicate that formed between the reacting oxide particles. Its use is undesirable, however, because it prevents the attainment of the full fluorescence that is characteristic of the pure silicate.

A still more interesting case of catalysis was shown in the effect of the volatile chlorides of potassium, sodium, zinc, and cadmium, although here again the fluorescence attained was below normal in brightness. Cad-

mium chloride was most effective. When two parts by weight of it were mixed with the reaction mixture and fired at $850^{\circ}\text{C}.$, the fluorescence rose to 75 per cent of its normal value after 70 min. The chloride by this time had completely evaporated. When the reaction mixture was fired at $850^{\circ}\text{C}.$ for the same period without the chloride, a product resulted whose fluorescence was only 3 per cent of normal. The catalytic effect persisted, though in lesser degree, with smaller amounts of the chloride, and was still well observable with only 1 per cent. Its basic effect lay in an acceleration of the reaction between the two oxides, as was demonstrated by firing them at $850^{\circ}\text{C}.$, before the addition of manganese but in the presence of cadmium chloride. The product was of course devoid of fluorescence.

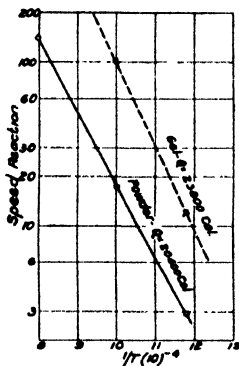


FIG. 1

FIG. 1. Heat of diffusion for mixtures containing zinc oxide, silica, and 0.4 per cent manganese

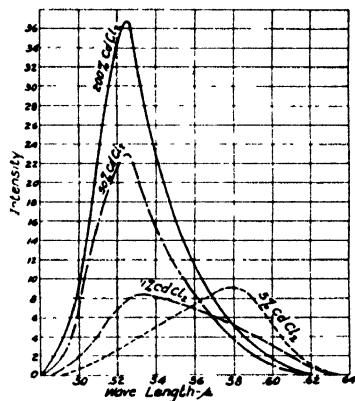


FIG. 2

FIG. 2. Spectral distribution of $\text{Zn}_2\text{SiO}_4 \cdot \text{SiO}_2 \cdot \text{Mn}$ prepared with cadmium chloride at $850^{\circ}\text{C}.$ Excited by 2536 Å.

When manganese oxide was added and the firing continued at $850^{\circ}\text{C}.$, fairly strong fluorescence, 15 per cent of normal, developed after half an hour. A blank mixture of zinc oxide, silica, and manganese dioxide gave no observable fluorescence whatever under the same firing.

The catalytic action of cadmium chloride consists, as in the case of a non-volatile flux, in dissolving away the silicate barrier between reacting particles. The low fluorescence of the final product is a result also of its transition through a solution phase. Both these effects were shown by an experiment with a normal phosphor which had acquired fully saturated fluorescence. This phosphor dissolved readily in the molten chloride. The product, on cooling, was non-fluorescent. The fluorescence reappeared after volatilization of the chloride, but was reduced 20 per cent below its original value. The highest fluorescence obtainable from firing

a mixture of oxides in the presence of the chloride was likewise 20 per cent below the normal value. This represents therefore an equilibrium value that was approached from each side,—solution of the silicate phosphor and synthesis of the phosphor from its constituent oxides. In neither case could the fluorescence be raised to normal by further firing at any temperature. The cause for the lower fluorescence lies in a reduction in grain size of the finished phosphor, an effect due to the solvent action of the flux, which will be discussed later.

In calculating the speed of reaction, use has been made of the fact that the fluorescence increases as the reaction progresses toward completion. At all periods of the uncatalyzed reaction, and at all temperatures of firing, the fluorescence, regardless of its intensity, had the same spectral distribution with only slight changes in the peak value. When a flux was present, the same situation held for temperatures of 1000°C. and higher. At 850°C., however, the first fluorescence that developed, as a result of an incipient reaction, had a distribution whose peak was shifted towards the red sufficiently to change the color. This effect was most marked in the case of cadmium chloride, no doubt because it is the strongest catalyst. Cadmium silicate, which has a pink fluorescence, was not formed in this reaction. This was shown by firing a mixture of silica, manganese, and cadmium chloride. The resulting product was non-fluorescent.

The curves of figure 2 represent the variations in spectral distribution that resulted from firing the mixture of oxides with variable amounts of the chloride. In each case the firing was continued long enough to volatilize the chloride completely. The intensity of fluorescence obtained was proportional to the amount of chloride introduced, for the mixture reacted at an appreciable rate only while the chloride was present. The distribution, obtained from the use of 5 per cent cadmium chloride, has a peak at 5800 Å. and its fluorescence is pink. This is in contrast to the phosphor obtained with 200 per cent cadmium chloride, whose peak is at the normal position of 5270 Å. and whose fluorescence is the normal green. The x-ray patterns of both were the same as that of the regular silicate phosphor. In this respect it is distinct from the red and yellow zinc silicates prepared by Gruhl (5) by firing above 1400°C. and quenching, for the crystal patterns of his products were altered, indicating that zinc silicate crystallizes in other modifications above 1400°C.

II. VARIATIONS IN COMPOSITION

Manganese concentration

A peak in the fluorescence intensity occurred at an optimum concentration of about 0.5 per cent manganese. As the manganese content rose, this peak was shifted slightly toward the red. These changes are brought out in table 2 and in the curve of figure 3.

The trend of the results has a definite significance. As Dr. Clarence Zener¹ has pointed out, it would be natural to expect an increase in fluorescence with increase in the concentration of manganese, until a disturbing influence sets in. Such an influence evidently begins at about 0.4 per cent manganese, and can be ascribed to the loss in energy of an excited manganese atom by collision with neighboring manganese atoms, as a consequence of the mobility allowed by thermal vibration. This would involve

TABLE 2

Dependence of fluorescence characteristics at 25°C. upon manganese content

MANGANESE	FLUORESCENCE	PEAK IN FLUORESCENCE
<i>per cent</i>	<i>per cent</i>	
0.01	12	
0.1	80	5270
0.4	96	5280
0.6	98	5290
0.9	100	5290
1.4	96	5310
2.0	90	5310
2.3		5330
4.5	44	5350
5.0	34	
9.0	3	

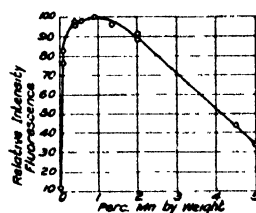


FIG. 3

FIG. 3. Variation in fluorescence at 25°C. of ZnSiO_3 , activated with manganese

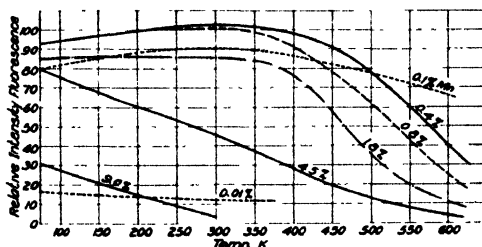


FIG. 4

FIG. 4. Variation in fluorescence of ZnSiO_3 , with temperature for various percentages of manganese

the emission of some of the energy of an excited electron in the infrared and a consequent shift of its emission in the visible toward the red. The actual occurrence of the latter is shown by the results of table 2.

This view is supported by measurements on the variation of fluorescence with temperature, made in collaboration with Dr. Zener. The results are shown in the curves of figure 4 for various specific concentrations of man-

¹ Dr. Zener's paper on this topic will be published in the near future.

ganese. The general increase in fluorescence that accompanies decreases in temperature is in accord with the conception of thermal vibration as an important factor. This view is strengthened by an observation of Dr. Zener's that the poisonous action of iron becomes less pronounced as the temperature is decreased. With 0.4 per cent iron the fluorescence, amounting only to 2 per cent at room temperature, had risen to 8 per cent at 77°K.

This relation between fluorescence and the concentration, C , of the activator (or of a dye, in the case of fluorescent solutions) has frequently been found to be expressed by the empirical equation of Bruninghaus (1)

$$F = Ace^{-nc}$$

The results of table 2 can be expressed by this equation only over the range 1.4 to 9.0 per cent manganese. For lower values of manganese content the fluorescence becomes increasingly higher than would be in accord with the equation.

X-ray examination produced evidence bearing upon the condition of the manganese within the silicate. Diffraction patterns were obtained through the courtesy of L. L. Wyman and E. T. Asp of this laboratory. On using CuK_α radiation and the method of back reflection, the same pattern was found for all zinc silicate phosphors, namely, a hexagonal structure, as shown in the photographs of figure 5. For manganese contents of 2 per cent and 5 per cent, however, the lattice spacing became increasingly greater. This can be observed for beams reflected through angles close to 180°, as represented in the photographs by the arc segments close to the central hole. It is evident that the manganese enters into solid solution with the zinc silicate, an atom of manganese being substituted for an occasional atom of zinc. The stretching of the lattice is a consequence of the larger ionic radius of the manganese, 0.91 Å., as compared with 0.83 for zinc (4).

A similar situation was found for the cadmium silicate phosphor, as illustrated in the x-ray diffraction patterns of figure 6. Here also the same pattern persisted in the presence of 5 per cent of the activator manganese. In this case, however, a reverse effect of the manganese is shown, —namely, a contraction of the lattice. This is evidence that the manganese has formed a solid solution likewise with the cadmium silicate, substituting for an occasional cadmium atom. The contraction is due to the smaller ionic radius of manganese as compared with that of cadmium, which is 1.03 Å.

Silica content

The concentration of silica proved to be important in its bearing upon the intensity of fluorescence, for it disclosed an unexpected effect; namely,

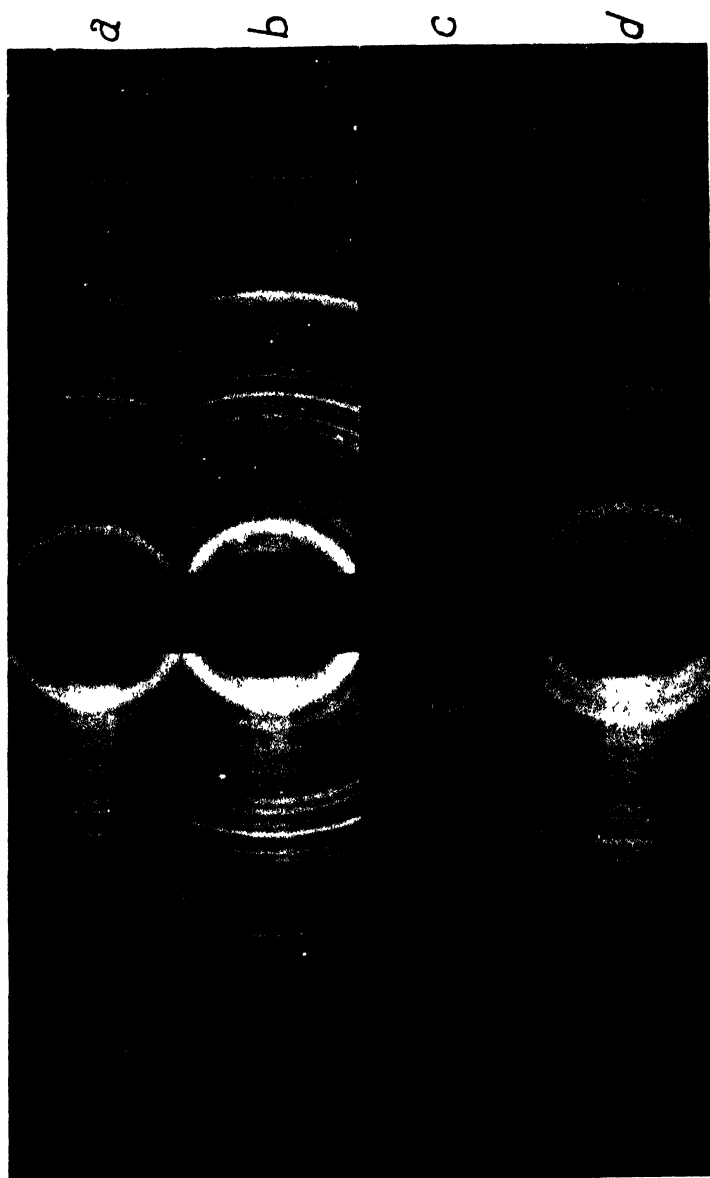


FIG. 5. X-ray patterns of Zn_2SiO_4 containing various amounts of manganese. Cu K_α radiation. a, 0 per cent manganese; b, 2.0 per cent manganese; c, 4.0 per cent manganese; d, 5.0 per cent manganese



FIG. 6. X-ray patterns of CdSiO_3 containing various amounts of manganese. $\text{Cu K}\alpha$ radiation. a, 0 per cent manganese; b, 5 per cent manganese

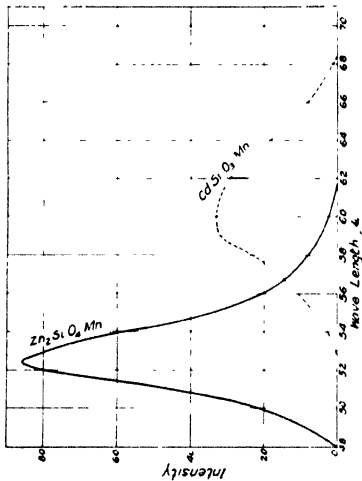


FIG 7

FIG. 7. Spectral distribution of fluorescence energy

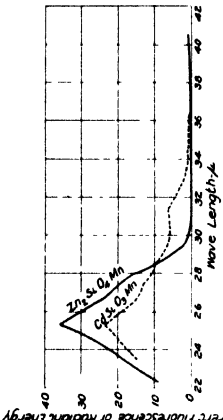


FIG. 8

FIG. 8. Efficiency of excitation

that the fluorescence is not reduced as the silicate is diluted with excess silica.

The thermal diagram for the system of zinc oxide and silica has been worked out by Bunting (2). It discloses only one compound, the ortho-silicate Zn_2SiO_4 , having the composition of the natural mineral, willemite, with a melting point of 1507°C . At 1432°C . there is a eutectic having the composition $\text{Zn}_2\text{SiO}_4 \cdot \text{SiO}_2$. This has frequently been called the meta-silicate, and its composition has been expressed by the formula ZnSiO_3 . Such a compound, however, appears not to exist, in the light of Bunting's work and of our own x-ray study, described below. It should therefore be considered as an agglomerate including 1 mole of silicate and 1 mole of free silica.

When the fluorescent orthosilicate was diluted with silica, the fluorescence of the mixture was found to decrease linearly, as would be expected. Firing of such mixtures brought about only insignificant increases

TABLE 3

Variation in fluorescence with silica content for 0.4 per cent manganese

COMPOSITION		FLUORESCENCE	
Molar per cent ZnO	Moles free SiO_2	I. Mechanical mixture: Zn_2SiO_4 , Mn + free SiO_2	II. Fired mixture of oxides
67	0	102	102
50	1	71	98
33	3		86
11	15	17	72

in fluorescence. On the other hand, the products obtained from firing mixtures of oxides rose almost to normal fluorescence, despite the presence of large excesses of free silica. This is brought out in table 3. Two series of mixtures were involved. The first (I of the table) was made up of the completed phosphor, $\text{Zn}_2\text{SiO}_4 \cdot 0.4$ per cent Mn, mixed with additional silica. The second (II) was prepared by mixing zinc oxide and silica in the desired proportion, adding 0.4 per cent manganese, and firing. The fluorescence remained approximately the same in mixture II whether the 0.4 per cent manganese was calculated for the orthosilicate content or for the combined content of the two oxides.

The reason for the continued high level of fluorescence of the products obtained by firing the mixture of oxides lies in the physical condition of the excess silica rather than in its incorporation into unique compounds. X-ray diffraction patterns were obtained both with MoK_α and CuK_α radiation, the latter by the method of back reflection. The same crystalline pattern persisted throughout, identical with that from precipitated zinc orthosilicate as well as with that from natural willemite. There was

no change in lattice parameter, such as would have resulted from a solid solution of silica in the silicate. On the contrary, the diffraction lines of free silica appeared in the pattern obtained for the phosphor with 33 molar per cent zinc oxide. They were absent for the composition of 50 per cent zinc oxide, containing 1 mole of free silica, but this is not surprising, because the x-ray scattering power of silica is much less than that of the compound Zn_2SiO_4 .

The conclusion is therefore that any excess silica is present as such. The condition of some of it is undoubtedly that of particles coated with a shell of silicate. It is probable, however, that some of it also is more intimately associated with the silicate and present as small colloidal groups scattered in a diffuse state throughout the mass, particularly at coarse lattice defects of the crystal. Such a view is, of course, speculative, but it is in accord with the localized segregations of colloidal sodium produced by Rexer (9) in crystals of sodium chloride. It would account, too, for the prolonged phosphorescence that occurs at an optimum concentration of one excess mole of silica per mole of compound. It is also in accord with results observed on grinding. When phosphors having a large excess of silica, 66 molar per cent or greater, were ground, the ultimate fluorescence attained was of the same order as that found for unfired mixtures of orthosilicate and silica. The effect of the grinding was obviously just to disintegrate the mass and to cause a dilution of the silicate with silica which had hitherto been intimately dispersed within the crystals. Refiring of such a mixture had no effect whatever in restoring its fluorescence.

III. ORIGIN OF FLUORESCENCE

From a consideration of the experiments that have been described on the characteristics of fluorescent zinc silicate, it would appear that the phenomenon of fluorescence is dependent upon the presence of manganese. This is borne out by the observations that fluorescence of appreciable magnitude does not arise in the absence of manganese, that manganese when present enters into the silicate molecule, substituting for a zinc atom, and that the resulting fluorescence is proportional to the manganese concentration up to an optimum value. The manner in which light may be emitted by excitation of the manganese can best be approached theoretically by a consideration of the energy states within a crystal. Unlike the states in a gas, these cannot be represented by discrete levels, because of the high concentration of atoms in a solid. The energy of valence electrons is so strongly influenced by the location of atomic nuclei and by the mutual presence and movement of other electrons, that the possible states are extended into bands, each one of which is characterized by a

finite range in energy. Furthermore, there are wide energy gaps between allowed bands.

Seitz and Johnson (11) have outlined a mechanism for the occurrence of fluorescence by excitation of impurity atoms in a crystal. It considers the localized, discrete energy levels that are introduced by the presence of a foreign atom at such low concentration that its proportion to the main atom of the crystal is far from a combining ratio. These discrete levels are found, if at all, within the forbidden zones, the gaps between the allowed energy bands. Excitation involves the ejection of an electron from one level to another, such, for instance, as the raising of an electron from one of these localized impurity levels to an upper unfilled band of the crystal. The spectrum of the fluorescence emitted by its return is continuous and of longer wave length than that of the exciting light by reason of several possible losses, including collisions with the lattice which cause some of the emission to be diverted to the infrared.

IV. ABNORMAL DECREASES IN FLUORESCENCE

Effect of grain size

In the discussion of reaction velocity, too large a size of the oxide particles was shown to be a factor which might prevent completion of the reaction and consequently limit the fluorescence of the product. Even after a complete reaction, however, the brightness of the fluorescence has been found to depend upon the crystal size of the finished phosphor.

Phosphors that exhibit greatest brightness have an average crystal size of about 4–5 μ with a maximum of about 13 μ and a minimum of about 1.5 μ . Aggregates of larger size, obtained by sintering the phosphor, have necessarily a reduced fluorescence, because the exposed surface of the powder per unit area covered by it becomes lower as the particle size is increased.

The grain size itself has been reduced in four ways: (1) by grinding in an agate mortar, (2) by reducing the temperature of formation from 1250° to 1100°C., (3) by preparation at 850°C. with cadmium chloride as catalyst, and (4) by fusion. In each case the fluorescence was lowered, even when the phosphor had the composition of the orthosilicate, a homogeneous compound devoid of free silica. The relation between grain size and fluorescence is shown in table 4. It is noteworthy that a refiring of the ground phosphor led to increases in both grain size and fluorescence, but failed to bring either to their original values.

There is a distinct tendency for the fluorescence to vary with the fineness of the material. The coarsest material has the highest fluorescence and the finest material has the lowest. Phosphors of intermediate crystal size show fluorescence whose brightness lies midway at values varying

according to the method of preparation. This relationship is in accord with the condition of the manganese atoms as affected by such changes in crystal size. As has already been pointed out, the fluorescence arises presumably from excitation of the manganese atoms. This process is possible, however, only for those atoms that find themselves incorporated within the interior of a crystal. The energy states of surface atoms are so different that the same phenomenon would not be expected. The smaller the crystal size, the greater will be the number of manganese atoms that occur on the surface of a crystal, rather than in its interior. This is more than a matter of probability of arrangement. The larger size of the manganese ion, together with its low percentage, implies that it produces localized stresses throughout the lattice. When a phosphor is ground, cracks will therefore occur most readily along planes including manganese atoms, and, consequently, more manganese atoms will find themselves on

TABLE 4

Relation between grain size and fluorescence of zinc orthosilicate with 0.4 per cent manganese

TREATMENT	DISTRIBUTION IN GRAIN SIZE				RELATIVE FLUORESCENCE
	7-14 μ	3-7 μ	1-3 μ	1 μ	
	per cent	per cent	per cent	per cent	
Prepared at 1250°C.	15	35	35	15	102
Prepared at 1250°C.; ground	0	0	5	95	32
Prepared at 1250°C.; ground and refired	0	8	22	70	81
Prepared at 1100°C.	0	5	80	15	76
Prepared at 850°C. with CdCl ₂ as catalyst	0	0	20	80	70
Prepared at 1600°C. by fusion.	0	5	80	15	67

external crystal surfaces than would be calculated from a probability rule of random distribution of cracks. A similar situation holds in the crystallization from a fused mass, for again boundaries between grains will form most readily along planes including the foreign atoms of manganese.

When the ground silicate was refired, the product proved to be highly sintered, in contrast to the pulverous condition of the original phosphor after its preparation at the same temperature; this is evidence of the much greater fineness of the ground product. The refiring produced a little grain growth—sufficient to raise the fluorescence somewhat—but both remained below the values characteristic of the original. The particularly low grain size of the product formed at 850°C. under the influence of the cadmium chloride flux is in accord with the trend observed at higher temperatures, where a reduction in grain size accompanied a reduction in the temperature of preparation.

The relation between fluorescence and grain size was confirmed by

microscopic examination of fluorescing particles. Those below $1.5\ \mu$ were by contrast so low in fluorescence as to appear almost dead. In another experiment samples of coarse and fine particles were collected by sedimentation of a normal phosphor in alcohol. At a 1 mm. thickness the fine particles were noticeably less bright than the coarse. Similar conclusions have been drawn by Riehl and Ortmann (10) from relations found between phosphorescence and grain size.

Effect of conversion to glass

Zinc silicate could not be converted into a glass, but this was done readily in the case of cadmium silicate by heating above its fusion temperature in a platinum crucible and cooling rapidly. In the absence of manganese, a clear white glass was formed. In the presence of 0.4 per cent manganese the glass was still clear, but was discolored a deep brown, in contrast to the white color of the crystalline product, and was devoid of fluorescence. Although the original powdered phosphor gave an x-ray diffraction pattern of lines characteristic of its crystalline structure, the glass showed no line pattern whatever. The loss of fluorescence on conversion to a glass has already been observed by Curie for zinc borate phosphors (3). He ascribed it to the change in condition from a crystalline to a glassy state. This is difficult to reconcile with the occurrence of a wide variety of fluorescent glasses the emitted light of which is dependent upon the presence of a trace of activating metal. Although in some cases such a metal forms fluorescent salts, such as the rare earths and the uranyl salts, yet many of them are common metals whose salts are devoid of fluorescence. It seems therefore more reasonable to conclude that the conversion of a phosphor, such as cadmium silicate, into a glass is accompanied by a decomposition of the fluorescent double silicate of cadmium and manganese into a conglomerate of cadmium silicate and manganese silicate which is non-fluorescent, just as any other mixture of these compounds would be. This view seems justified by the change in color, for manganese silicate is a deep brown. It seems justified also by the diversity in size of the metal ions, cadmium and manganese.

Further evidence is shown by the behavior of the glass when refired below its melting point. When the temperature was $100^{\circ}\text{C}.$ below the normal firing temperature, the mass crystallized and developed a low fluorescence. Even after 65 hr. of firing, however, the fluorescence remained low and some of the brown discoloration persisted. This is hardly in accord with what one would expect if the return to a fluorescent phosphor involved simply the transformation from the glassy to the crystalline state. It would seem rather to denote a reaction involving the diffusion of two separate silicates to form the double silicate characteristic of the phosphor. When the glass was refired directly at the normal firing

temperature, it was reconverted into the normal white phosphor and developed a relatively bright fluorescence. This fluorescence was still from 20 to 30 per cent below the original value. Examination showed the grain size to be of the order of that noted in table 4 for fused zinc silicate. The reduction is therefore the normal one that is dependent upon the reduction in grain size.

It is not surprising to find a similar effect produced by the action of a flux capable of converting a phosphor into a glass at temperatures below its normal melting point. This could be done with zinc silicate by firing at 1000°C. with a sufficient amount of sodium borate, zinc borate, or zinc phosphate. The glass obtained was non-fluorescent. With sodium borate a glass was obtained even at 50 per cent mixtures. It was violet in color, denoting as before a decomposition of the phosphor as the cause for the loss of fluorescence. When this glass was fired for 15 hr. at 750°C., it devitrified into a crystalline product and developed the characteristic fluorescent spectrum of zinc silicate with an intensity 9 per cent of normal.

V. EXCITATION

The two silicate phosphors, together with some sulfide phosphors, were examined for their luminous characteristics by Frank B. Quinlan and the author. The spectral distribution was found with a spectrophotometer, and the efficiency of excitation was determined under radiation from a monochromator, measuring the radiant energy of a line with a thermopile and the fluorescence lumens in a 4.5-cm. sphere with a photovoltaic cell and correcting filter. The lumens were converted into energy units by calibration of the sphere for visible light of various wave lengths. The efficiency represents, therefore, the percentage which the fluorescence energy within the visible range bears to the radiant energy. The results are given in table 5. The silicates contain 0.4 per cent manganese. The two sulfides are commercial products and presumably contain copper as an activator. The uranyl salt is potassium uranyl sulfate. The spectral distribution and excitation of the silicate phosphors are shown graphically in figures 7 and 8.

No data were obtained on the absorption of ultraviolet light by the phosphors. It is interesting, however, to consider the quantum yield in terms of the quanta of radiant energy necessary to yield one quantum of fluorescence energy. This is done in table 6 for those wave lengths at which the efficiency was particularly high.

In order to have a photographic record of the efficiency of excitation, the Duclaux and Jeantet method was resorted to (6). A phosphor was coated on the outer surface of a plate of glass. This was placed over a photographic plate with a No. 16 Wratten filter in between. The combination absorbed all radiation below 5461 Å., except that of 3125 Å., a

small amount of which was transmitted. Consequently the photographic plate recorded only the fluorescent light, and displayed a pattern of lines corresponding in position with the ultraviolet lines that were capable of exciting fluorescence. Their relative intensity is a measure of the degree of excitation. The attached photographs in figure 9 bring out, for instance, the strong contrast between the two silicates, excited only by the far ultraviolet, and the group of the sulfide and uranyl salts excited most strongly by the near.

TABLE 5

Percentage of fluorescence energy in visible in relation to energy of exciting line

LINE	Zn ₂ SiO ₄	CdSiO ₃	ZnS	ZnCdS	UO ₂ SO ₄
A.	per cent	per cent	per cent	per cent	per cent
2225	8		1		
2378	20	16			
2399	22	18	11	4	14
2483	30	21	15	8	18
2536	36	24	17	10	19
2652	25	16			
2699	22	14			
2753	19	13	20	8	17
2803	15	11	22		
2893	6	9	23		
2967	1	7	23	14	22
3126	0	6	25	17	18
3341	0	1	43	18	21
3651	0	0	64	42	26
4047	1	1	67	57	39

TABLE 6

Quanta of radiant energy for quantum of fluorescence energy

PHOSPHOR	2536 A.	3651 A.	4047 A.
Zn ₂ SiO ₄	1.3		
CdSiO ₃	1.8		
ZnS	2.8	1.1	1.1
ZnCdS	1.2	1.4	1.2
UO ₂ SO ₄	2.5	2.6	1.9

SUMMARY

A zinc silicate phosphor, as well as related ones, can be prepared by firing mixtures of the constituent oxides, with manganese as activator. The reaction is a diffusion phenomenon having a heat of diffusion of 20 to 24 Cal. Its speed depends upon the particle size of the oxides and can be accelerated by the addition of those inert substances capable of dissolving away the barrier shell of silicate as formed.

Fluorescence depends upon the presence of manganese. At an optimum concentration of 0.4 per cent manganese it shows a peak at all temperatures and remains almost constant from 100°C. to 77°K. For any concentration above 0.4 per cent manganese the fluorescence increases continuously as the temperature is reduced, approaching the value of the optimum at 77°K. The fluorescence is at a peak for the composition of the orthosilicate but is reduced only slightly when prepared with large excesses of silica. Such phosphors are disintegrated readily by grinding and are simply conglomerates. X-ray examination shows a persistence of the orthosilicate structure throughout. It shows also a stretching of the lattice in the presence of manganese, denoting that the latter enters into the silicate structure by substitution for an occasional zinc atom.

Reductions in fluorescence resulting from fusion or from grinding, even when followed by refiring, are due to permanent reductions in crystal size. The complete loss of fluorescence produced by conversion into a glass is a consequence of a decomposition of the double silicate into its constituents. The fluorescence is partially restored by refiring at a temperature below the fusion point.

The efficiency of excitation was measured between 2225 Å. and 4047 Å. for some silicate and sulfide phosphors. Several of them showed a quantum efficiency of nearly unity for specific wave lengths.

The author is indebted to William H. Tomb, Elwood M. Douthett, and Robert I. Reed for their assistance in preparing the phosphors.

REFERENCES

- (1) BRUNINGHAUS, L.: *Compt. rend.* **149**, 1375 (1909).
- (2) BUNTING, E. N.: *J. Research Natl. Bur. Standards* **4**, 134 (1930).
- (3) CURIE, M.: *Compt. rend.* **203**, 996 (1936).
- (4) GOLDSCHMIDT, V. M.: *Trans. Faraday Soc.* **25**, 282 (1929).
- (5) GRUHL: *Handbuch der Physik* **23**, 571 (1926).
- (6) HEYNE, G., AND PIRANI, M.: *Z. techn. Physik* **14**, 31 (1933).
- (7) JANDER, W.: *Z. anorg. Chem.* **163**, 1 (1927); **200**, 245 (1931); **226**, 225 (1936).
- (8) LENARD, P., SCHMIDT, F., AND TOMASCHEK, R.: *Handbuch der Experimental Physik*, Vol. XXIII, Part I, p. 456 (1928).
- (9) REXER, E.: *Z. Physik* **76**, 735 (1932).
- (10) RIEHL, N., AND ORTMANN, H.: *Ann. Physik* **29**, 556 (1937).
- (11) SEITZ, F., AND JOHNSON, R. P.: *J. Applied Physics* **8**, 255 (1937).
- (12) UYTERHOEVEN, W., AND HESS, K. W.: *Elektrische Gasentladungslampen*, p. 322. J. Springer, Berlin (1938).

ADSORPTION ON HETEROPOLAR SURFACES¹

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INTRODUCTION

The properties of the solid-liquid interface have received much attention recently because of their direct application to problems such as flotation and lubrication in many industrial fields. Although the phenomena encountered in these fields are explainable in terms of the theory of this interface, theoretical investigations of the interface have lagged far behind the practical applications. This is because the complexity of the solid surface introduces numerous experimental difficulties in any study of the solid-liquid interface.

One of the most obvious phenomena connected with the solid-liquid interface is the liberation of heat when such an interface is formed. This is usually called the heat of wetting or the total energy of immersion. The literature contains much work on the heats of wetting, but a great deal has been done on silica gel and charcoal. Since these substances possess minute capillaries in which adsorption takes place, they present phenomena entirely different from and more complex than those obtained when impenetrable crystalline particles are used. This paper has been restricted to the latter materials, since a study of such systems will probably throw more light on the nature of the solid-liquid interface. In particular, the heats of wetting of silica, calcium fluoride, lead sulfate, and barium sulfate powders by water and by methyl, ethyl, propyl, isopropyl, and butyl alcohols have been determined.

BRIEF RÉSUMÉ OF EARLIER WORK

In 1822 Pouillet (16) observed that heat is evolved when finely powdered solids are wet by liquids. Four liquids—alcohol, oil, ether, and water—were used with various solids,—metals, oxides, glass, porcelain, silica, and sulfur. He connected the heat effects with physical phenomena, such as capillarity.

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Thirty years later Tate (18), on the basis of his experiments, concluded that chemical action at the interface was the explanation for liberation of heat. Maschke (13) attempted to account for it on the basis of friction between the liquid and solid. Rose (17) and Jungke (9) agreed that solids condense a layer of liquid upon them under compression and that a heat of compression was liberated. Lamb and Coolidge (11) have had much success with the compression theory in explaining heats of wetting of charcoal by various vapors.

Martini (12) and Cantoni (3) agreed on the solid solution theory, reasoning that, just as solids are dissolved by liquids and thereby become liquid, so water may be dissolved by silica and thereby become solid.

Gaudechon (4) believes the heat of wetting to be due to association or polymerization of molecules of liquid in contact with a solid.

Patrick and Grimm (15) have considered the heat of wetting of silica gel from the standpoint of surface energy changes involved. They distinguish between capillary adsorption and adsorption on a plane surface. The initial film of adsorbed liquid is admitted to be under compression, but is held to be negligible in amount as compared with the total condensation in a solid having capillary structure. Harkins and Ewing (7) have obtained direct experimental evidence of the compression of the layer of organic liquids adsorbed on activated charcoal.

Bartel and coworkers (1) have conducted extensive researches on solid-liquid interfaces, measuring the adhesion tension (free energy of adsorption) by a very ingenious method. de Boer and coworkers (2) have done considerable work on the adsorption of dipoles on calcium fluoride and have used electrostatic equations to interpret their results. Illiin (8) and coworkers have had a measure of success in calculating the heat of wetting barium sulfate by water by use of the formula

$$E = \frac{N\mu\Sigma e}{r_0^2}$$

where E is the potential of adsorption, N the number of lattice ions per square centimeter, Σe the charge on the lattice ion, r_0 the equilibrium distance from the center of the lattice ion to the center of the dipole, and μ the dipole moment.

THEORETICAL

The adsorbed dipole on a heteropolar surface has been pictured as an oscillating molecule, oscillating about an equilibrium position, r_0 , the distance of the center of the lattice ion from the center of the dipole. This equilibrium position is maintained by two opposing forces, one attractive, the other repulsive.

In figure 1, C, D, and B represent the centers of lattice ions on a portion

of a heteropolar crystal surface, and A represents the center of a dipole adsorbed on the positive ion whose center is C. In general then, letting $ad = r$, where r is the distance of the center of the lattice ion from the center of the dipole at any point of its oscillation and d is the lattice constant, the attractive energy is

$$E_1 = \frac{\mu Ze}{a^2 d^2}$$

where μ is the dipole moment, Z the valence of the lattice ion, and e the electrostatic charge.

This may be summed up over the surface. For the first three charges the energy terms will be

$$E_1 = \frac{\mu Ze}{a^2 d^2}; E_2 = \frac{-\mu Ze}{AD^2} \cos DAC; E_3 = \frac{\mu Ze}{AB^2} \cos BAC$$

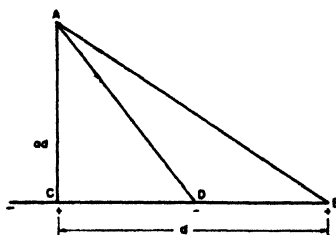


FIG. 1. Forces acting on an adsorbed dipole

Summing over the entire surface we obtain as the attractive energy of an oscillating dipole adsorbed on a heteropolar crystalline surface

$$E_1 + E_2 \cdots E_n = E' = \frac{\mu Zea}{d^2} \sum (-1)^{2(n+m)} [a^2 + n^2 + m^2]^{-3/2}$$

wherein $m = c/2$ and c takes on all integer values positive and negative and 0. For the energy of adsorption at the equilibrium position this becomes

$$E'_0 = \frac{\mu Zea_0}{d^2} \sum (-1)^{2(n+m)} [a_0^2 + n^2 + m^2]^{-3/2}$$

where $a_0 d = r_0$.

The repulsive energy will be in the form:

$$E'' = \frac{b}{(ad)^p}$$

where b is a constant, and p is greater than 2 and in all probability is of the order of 10. The repulsive terms arising from charges other than the

primary one upon which the dipole is adsorbed may be neglected because of this large exponent.

Therefore we may write as the complete expression for a dipole on a crystal surface:

$$E' + E'' = E = \frac{\mu Zea}{d^2} \sum (-1)^{2(n+m)} [a^2 + n^2 + m^2]^{-3/2} - \frac{b}{(ad)^p}$$

This expression neglects such secondary effects as induction, interaction between dipoles, and lattice layers other than the first.

If we wish to take account of layers other than the first, the expression becomes

$$E = \frac{\mu Ze(a+q)}{d^2} \sum (-1)^{2(n+m)+q} [(a+q)^2 + n^2 + m^2]^{-3/2} - \frac{b}{[(a+q)d]^p}$$

where q is 0 for the first layer, 1 for the second, etc.

This expression may be used for calculating the energy of adsorption of powders of known area of the sodium chloride type, wherein the naturally occurring faces are all identical.

EXPERIMENTAL

A. Preparation of powders

(1) *Silica*. Silica sand was put through a disc mill several times. The resulting product was grey in color, as it contained considerable quantities of iron from the grinder plates. It was treated several times with a mixture of strong nitric and hydrochloric acids to dissolve this iron. The silica was then washed by decantation with distilled water at frequent intervals for a period of 3 weeks. It was then dried and ignited to drive off residual water and carbon, which remained after the solution of the iron. A pure white material was obtained which, however, was not fine enough for determination of heats of wetting; therefore it was ground wet in a porcelain ball mill for a period of 24 hr. The resulting product was dried and ignited. Accurately weighed quantities of this material were placed in thin glass bulbs, sealed to a vacuum apparatus, and heated to 400°C. for 24 hr. *in vacuo*.

(2) *Fluorite*. Very pure powdered fluorite was obtained from the Rosiclare Lead and Fluorspar Mining Company and was ground in the ball mill similarly to the silica, dried at 110°C., and heated *in vacuo* just below 400°C.

(3) *Lead sulfate*. Pure crystalline lead sulfate was prepared by adding 6 *N* sulfuric acid to a saturated solution of lead nitrate, followed by washing by decantation until free from acid. It was heated in thin glass bulbs

in vacuo to 200°C. Above this point sintering occurred. This was the method used by Koehler and Matthews (10).

(4) *Barium sulfate*. Barium sulfate was prepared by the method of von Weimarn (19), which gave a pure crystalline product. To a 0.2 *N* solution of barium thiocyanate a saturated solution of manganous sulfate was added. The precipitate was washed by decantation, dried at 110°C., and heated *in vacuo* to 200°C.

B. Purification of alcohols

The c. p. alcohols were refluxed and distilled over lime, the first and last portions being rejected.

C. Apparatus

The apparatus for the evacuation of the powders consisted of a vacuum oil pump, a mercury diffusion pump, and a small electrical resistance furnace for heating the bulbs of powder.

The calorimeter itself consisted of a Dewar flask with an especially designed brass top to which the flask was fastened. The temperature rise caused by the heat of wetting was determined with the aid of a 36-junction copper-Constantan thermopile. Each junction was insulated by dipping it into a dilute solution of Duco cement in acetone and drying it. The thirty-six hot junctions were inserted into an 8-mm. Pyrex tube and just brought into contact with a thin glass membrane at one end of the tube, the tube then being filled with paraffin. The cold junction was constructed similarly. This thermopile could be used in any type of solution without fear of damage. The sensitivity was such that 148 microvolts was equivalent to 0.1°C. The calorimeter was electrically calibrated by a nichrome heating coil. The E.M.F. across the coil was measured and the current in the coil measured by determining the drop across a standard 1-ohm resistance in series with the circuit.

The constant-temperature bath in which the calorimeter was immersed was held at 25°C. The cold junction of the thermopile was also immersed in a Dewar flask and maintained at 25°C. in the bath.

D. Procedure

The procedure for the determination of the heats of wetting was as follows: The sample of the powder in the thin glass bulb was placed in a holder in the calorimeter, and the calorimeter, filled with 300 cc. of liquid, was clamped into position. The constant-temperature bath was regulated to 25°C. and the Dewar flask, containing the cold junction of the thermopile, filled with water at this temperature. Twenty-four hours was allowed to reach equilibrium. The calorimeter stirrer was started, and

the electrical heater was used to bring the temperature of the calorimeter to that of the cold junction. Ten minutes before the bulb was broken temperature readings were taken at 1-min. intervals in order to determine the rise in temperature due to stirring. The bulb of powder was then broken by means of a rod inserted through the hollow stirrer shaft, and temperature readings were taken every minute. The heat of wetting was usually completely liberated in 3 min. After temperature readings were taken for 5 min., the heating coil was connected for exactly 1 min., the current and voltage being measured. The temperature rise was again measured by the thermopile. By comparison with this temperature rise, produced by a known quantity of heat from the heating coil, the heat evolved during the wetting process was calculated.

At least five determinations of the heats of wetting of each powder by each liquid were made; they agreed within approximately ± 0.01 cal. per gram of powder.

RESULTS AND DISCUSSION

As shown in table 1, the heats of wetting of calcium fluoride and lead sulfate by water and by methyl, ethyl, propyl, isopropyl, and butyl alcohols are zero. The result on lead sulfate is in agreement with the work of Koehler and Matthews (10), who have previously found that the heat of wetting of lead sulfate by water is zero. On the basis of any electrostatic theory of adsorption it is difficult to explain the wide variance between barium sulfate and lead sulfate, since they have the same crystal structure, their lattice constants are very close to each other, and their negative ions are identical. The greatest difference is in the radii of the metallic ions,—lead ion = 0.85 \AA . and barium ion = 1.43 \AA . This, if anything, should make dipole adsorption of somewhat greater energy on the lead ion. This is an anomaly which needs further work for explanation. It is believed, however, that it is probable that the surface has been altered in some manner, possibly by the reaction with adsorbed water during drying. de Boer and Dippel (2) have presented evidence to this effect in the case of calcium fluoride, which reacted with adsorbed water while drying *in vacuo* above 400°C . to form $\text{Ca}(\text{OH})\text{F}$ and HF . In other words, calcium fluoride and lead sulfate may not adsorb water in the ordinary manner, but may form some sort of definite hydrate which is not removed by ordinary treatment, and which, consequently, prevents further appreciable adsorption when these powders are immersed in liquid.

The reason for using the homologous series of alcohols for determinations of heats of wetting is because they all have the same dipole moment within the limits of experimental error, namely 1.6×10^{-18} e.s.u. (5). The experimental values obtained give some information as to the orientation

of the adsorbed molecules when considered in the light of the dipole theory of adsorption; wherein the potential of dipole is given by the formula:

$$E = \frac{\mu Ze}{r^2}$$

If all the hydroxyl groups were oriented towards the crystal surface, one would expect all the alcohols from methyl through butyl to have practically the same energy of adsorption. Since this is not the case, we make the assumption that the hydroxyl group is oriented towards the crystal surface when it is adsorbed on the positive ions, and reverses itself on the negative ions. Adsorption then on negative ions is weak and orientation is probably much less pronounced than on the positive ions.

The decrease in heats of wetting of silica gel as one ascends the homologous series of alcohols has been explained by increasing steric hindrance in the fine capillaries of the gel. Although there are probably many surface cracks on the silica that we have prepared by grinding, the hindrance

TABLE 1
Average values of heats of wetting in calories per gram

LIQUID	SiO ₂	CaF ₂	PbSO ₄	BaSO ₄
Water	1.00	0	0	0.49
Methyl alcohol	0.69	0	0	0.24
Ethyl alcohol	0.65	0	0	0.22
<i>n</i> -Propyl alcohol	0.60	0	0	0.19
<i>n</i> -Butyl alcohol	0.50	0	0	0.16
Isopropyl alcohol	0.63	0	0	0.21

due to these is small in comparison with capillary hindrance, and the barium sulfate is no doubt more free from surface cracks than the silica.

In the case of isopropyl alcohol the hydroxyl group is attached to the center carbon atom; such a molecule adsorbed with the hydroxyl group oriented towards the crystal surface covers more surface area than a primary alcohol. One might be led to suspect that there would be hindrance to the placing of such molecules, one on each lattice ion. The amount of hindrance would, of course, depend upon the magnitude of the lattice constant, *d*. No sharp decrease in the heat of wetting of isopropyl alcohol over those of the primary alcohols was observed, which seems to indicate that no such hindrance took place in the surfaces of those solids investigated.

Approximate curves (figures 2 and 3) have been calculated and drawn for the energy of adsorption of water and of methyl, ethyl, propyl, and butyl alcohols on barium sulfate, using the formula:

$$E = \frac{\mu Ze}{r^2} - \frac{b}{r^{10}}$$

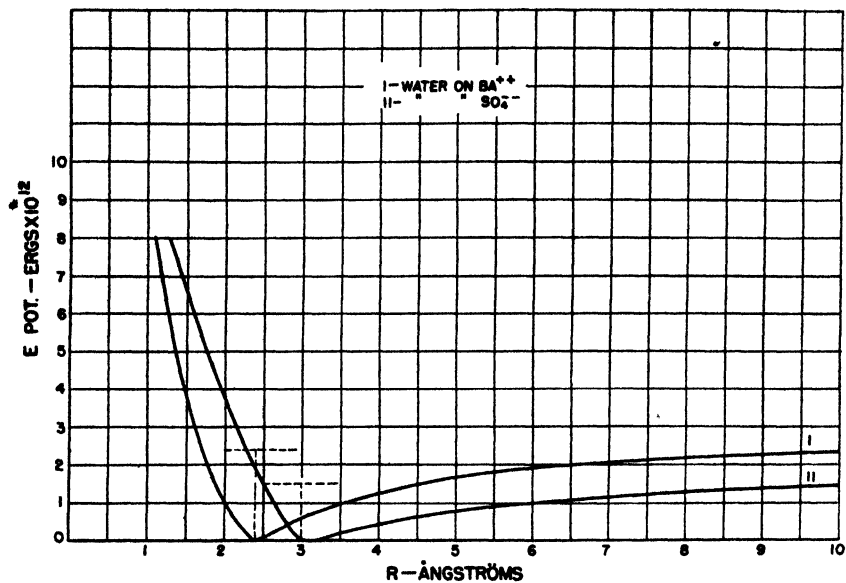


FIG. 2. Energy of adsorption of water on barium sulfate

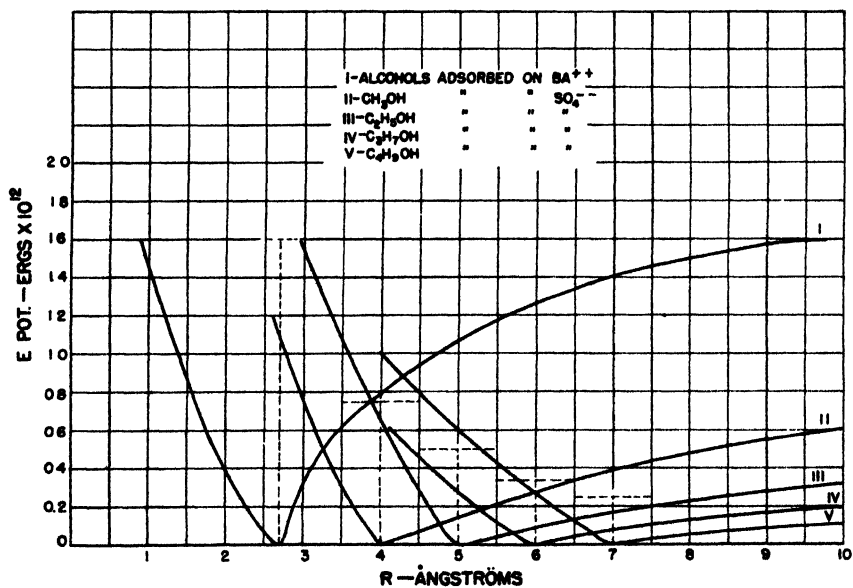


FIG. 3. Energy of adsorption of alcohols on barium sulfate

b is determined in the usual manner by setting the derivative of the above expression equal to 0 and giving r its equilibrium value.

It has been assumed that the energy of adsorption on the barium ion is the same regardless of the alcohol, since they all have the same dipole moment. Energy of adsorption on the sulfate ion decreases as one ascends the series, because the dipole is farther removed from the ion; also, the displacements from the equilibrium position become greater. The energy of binding on the sulfate ion is so small that actually it is quite probable that orientation is much less pronounced there than on the barium ion and that the average life period of an adsorbed molecule is very short. These calculations are intended to be only approximate, but it is believed that they represent the general trend of conditions on heteropolar surfaces.

TABLE 2

Comparison of experimental and theoretical values of heats of wetting in calories per gram

LIQUID	SiO ₂		BaSO ₄	
	Experimental	Theoretical	Experimental	Theoretical
Water	1.00	1.00	0.49	0.49
Methyl alcohol	0.69	0.61	0.24	0.28
Ethyl alcohol	0.65	0.55	0.22	0.25
n-Propyl alcohol	0.60	0.52	0.19	0.23
n-Butyl alcohol	0.50	0.50	0.16	0.21

TABLE 3

Comparison of experimental and theoretical value of heats of wetting in calories per gram

LIQUID	MgO		ZnO		TiO ₂	
	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical
Water.	1.00	1.00	1.00	1.00	1.00	1.00
Butyl alcohol			0.58	0.51	0.66	0.55
Amyl alcohol.	0.50	0.46				

With water as a standard, table 2 compares the experimental heats of wetting and those obtained by use of the formula:

$$E = \frac{\mu Ze}{r_0^2} - \frac{b}{r_0^{10}}$$

This formula was found to be an excellent first approximation to the more complete formula

$$E = \frac{\mu Zea}{d^2} (-1)^{2(n+m)} [a^2 + n^2 + m^2]^{-3/2}$$

derived on page 581. The sum of the two energies of adsorption (on the positive and negative ions) is taken as proportional to the total energy of adsorption.

Table 3 gives similar results, using the data of Harkins and Dahlstrom (6) for the heats of wetting of titanium dioxide and zinc oxide by water and butyl alcohol, and the data of Meissner (14) for the heats of wetting of magnesium oxide by water and amyl alcohol, all on the basis of water = 1.00.

SUMMARY

1. The heats of wetting of silica, calcium fluoride, lead sulfate, and barium sulfate by water and by methyl, ethyl, propyl, isopropyl, and butyl alcohols have been determined.
2. An explanation for the zero heats of wetting of calcium fluoride and lead sulfate has been offered.
3. A general theory for the adsorption of dipoles on heteropolar surfaces has been presented.
4. Simple theoretical calculations of the heats of wetting of barium sulfate and silica have been shown to be in fair agreement with experimentally determined values.

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REFERENCES

- (1) BARTEL AND FU: Colloid Symposium Monograph 7, 135 (1936).
BARTEL AND OSTERHOF: Colloid Symposium Monograph 5, 113 (1927).
- (2) DE BOER AND DIPPPEL: Z. physik. Chem. **B25**, 399 (1934).
- (3) CANTONI: Rend. ist. lombardo sci. **8**, 135 (1866).
- (4) GAUDECHON: Compt. rend. **157**, 209 (1913).
- (5) GROVES AND LUGDEN: J. Chem. Soc. **1937**, 158.
- (6) HARKINS AND DAHLSTROM: Ind. Eng. Chem. **22**, 892 (1930).
- (7) HARKINS AND EWING: J. Am. Chem. Soc. **43**, 1795 (1921).
- (8) ILLIIN AND COWORKERS: Phil. Mag. **153**, 294 (1937).
- (9) JUNGKE: Ann. Physik u. Chemie **125**, 292 (1865).
- (10) KOEHLER AND MATTHEWS: J. Am. Chem. Soc. **46**, 1158 (1924).
- (11) LAMB AND COOLIDGE: J. Am. Chem. Soc. **42**, 1146 (1920).
- (12) MARTINI: Atti ist. Veneto sci. **8**, 102 (1896).
- (13) MASCHKE: Ann. Physik u. Chemie **146**, 431 (1872).
- (14) MEISSNER: Ann. Physik u. Chemie **29**, 114 (1886).
- (15) PATRICK AND GRIMM: J. Am. Chem. Soc. **43**, 2144 (1921).
- (16) POUILLET: Ann. chim. phys. **20**, 141 (1822).
- (17) ROSE: Ann. Physik **73**, 1 (1847).
- (18) TATE: Phil. Mag. **20**, 508 (1860).
- (19) VON WEIMARN: J. Russ. Phys. Chem. Soc. **40**, 125 (1908).

COPPER AS CATALYST FOR THE HYDROGENATION OF BENZENE

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INTRODUCTION

In 1905 Sabatier and Senderens (16) concluded that copper was unable to catalyze the hydrogenation of benzene. Twenty years later, Pease and Purdum (13) reported the hydrogenation of benzene at ordinary pressure in the presence of copper as catalyst. We have reinvestigated this problem and have found that pure copper can just barely hydrogenate benzene at ordinary pressure but that it readily does so under superatmospheric pressure.

The authors have found that the hydrogenating activity of copper is so susceptible to impurities that the purity of each sample must be confirmed by spectrographic analysis. Their experiments show that small amounts of nickel, chromium oxide, etc. activate copper sufficiently to enable it to hydrogenate benzene at ordinary pressure. For example, the presence of 0.007 per cent of nickel (1 nickel atom per 13,000 copper atoms) makes it possible for copper to hydrogenate benzene to the extent of 8 per cent in a contact time of 180 sec. With 0.01 per cent and 0.04 per cent of nickel, benzene is hydrogenated 21 per cent and 36 per cent, respectively. On the other hand, traces of certain other impurities, as, for example, lead, poison the copper catalyst so that it can not hydrogenate benzene even under superatmospheric pressure.

Pease and Purdum apparently assumed that nickel and cobalt were the only pertinent impurities. They reported that their copper catalyst was free from nickel and cobalt, but that it contained a trace of iron. They gave no information as to their method of analysis or as to its accuracy.

In order to ascertain whether copper can catalyze the hydrogenation of benzene it was first necessary to prepare pure copper catalyst. Numerous samples of copper oxide and copper carbonate were analyzed; all were found to be impure. Pure copper preparations were finally obtained by precipitation.

The final step in the preparation of copper catalyst was the reduction of copper oxide by hydrogen. The hydrogenating activity of the reduced catalyst was evaluated by passing a mixture of 6 to 7 volumes of hydrogen

and 1 volume of benzene over it at 225°C. and ordinary pressure and determining the amount of cyclohexane in the product.

Pure copper catalyst was usually prepared by the decomposition and reduction of basic copper carbonate, which had been precipitated from the nitrate by ammonium carbonate. Spectroscopic examination showed that the reduced copper contained less than 0.005 per cent of nickel, cobalt, iron, lead, or tin, and not more than 0.01 per cent of aluminum, chromium, calcium, or magnesium. Electrolysis, however, revealed the presence of not less than 0.2 per cent of oxygen. Such copper, containing oxygen, catalyzed the hydrogenation of benzene at ordinary pressure and 225°C. with difficulty (1 per cent hydrogenation in 300 sec. contact time), but it readily hydrogenated benzene at 350°C. under a pressure of 150 atm. of hydrogen.

Pure copper was also prepared by the method of Ipatieff and Werchowsky (11, 10), which consists in the reduction of copper ions by hydrogen under pressure. The original copper sulfate was purified by recrystallization, followed by precipitation with hydrogen sulfide and subsequent conversion of sulfide to sulfate by nitric acid. The metallic copper precipitated by hydrogen analyzed 100.00 ± 0.05 per cent pure by electrolysis, and the spectroscope showed it to be as free from other metals as the sample described above. This copper did not hydrogenate benzene at ordinary pressure and 225°C. or even under 150 atm. of hydrogen at 350°C. However, a copper preparation obtained by reworking this inactive copper (solution in nitric acid, precipitation as carbonate, decomposition, and reduction) was able to hydrogenate benzene under superatmospheric pressure.

In view of the fact that 100.0 per cent copper precipitated by hydrogen in the form of large microcrystals did not hydrogenate benzene, whereas 99.7 per cent copper prepared from basic carbonate, containing oxygen as impurity, and possessing a structure on the borderline between crystalline and colloidal according to its x-ray picture, did hydrogenate benzene, the following questions arise: Is the inactivity of the first type of copper due to insufficient surface area, or is the catalytic activity of the second type of copper due to the activating effect of oxygen and/or water?¹

The net result of a catalytic process such as the hydrogenation of benzene in the presence of copper is due to the combined effect of many variables. These variables fall into two main divisions: (1) the experimental conditions of precipitation, of reduction of the oxide, and of hydrogenation of the benzene, and (2) the properties of the catalyst, such as chemical composition, development of internal structure, and stability of lattice. It is only when all of these conditions are favorable that the best results can be expected.

* ¹ See Ipatieff on the rôle of oxides in catalysis (8).

The system copper-benzene-hydrogen is an excellent one for the study of the variables of hydrogenation catalysis, since the intrinsic hydrogenating ability of copper with regard to benzene is so slight that the importance of these variables is magnified. With an active catalyst such as nickel, which when properly prepared and promoted (9) is able to hydrogenate benzene quantitatively at 50°C. and ordinary pressure in a contact time of 1 sec., it is far more difficult to separate and evaluate the many variables which contribute to hydrogenation catalysis.

In this study of the catalytic properties of copper one variable was changed at a time, the other variables being held constant and favorable for the hydrogenation of benzene. Thus it was possible to determine the separate effects of the variables concerning the preparation and properties of copper hydrogenation catalyst.

With a sample of copper oxide which contained about 0.1 per cent of nickel we studied the effect of the time-temperature conditions of reduction. The threshold temperature at which copper catalyst rapidly loses activity is 350-400°C.

The hydrogenating activity of copper catalysts can be estimated by microscopic examination of the surface. The catalytically active surface is a spongy structure of microcrystals with many fissures between the individual crystals. Three types of inactive surface are distinguishable under the microscope: (1) smooth, compact, and without crystal faces; (2) composed of smooth, round particles; and (3) made up of large microcrystals.

Application of the radioactive emanation method made it possible to correlate the emanating power (and therefore surface) of the copper catalysts with hydrogenating activity. A copper catalyst which contained 3.5 per cent of chromium oxide and whose relative hydrogenating activity was 28 at 90 sec. contact time was found to possess thirty-nine times as much emanating power as a preparation of pure copper whose relative hydrogenating activity was 0. However, loss in catalytic activity due to heating at 400°C. could not be directly correlated with the change in emanating power.

EXPERIMENTAL

Preparation and testing of copper catalysts

Preparation of copper catalysts. The first copper catalysts, which were prepared by the reduction of c.p. copper oxides and carbonates, hydrogenated benzene at 225°C. and ordinary pressure to the extent of 30 to 50 per cent, in a contact time of 90 sec. However, these copper catalysts were all contaminated with other metals, sometimes to as high as 0.2 per cent. The most common activating impurity was nickel. *

Preparation of pure copper catalyst from basic carbonate and hydroxide.

Precipitation was usually made with ammonium carbonate or hydroxide, the former being preferable. The precipitate was washed once, and the residual ammonium nitrate was removed by heating. Sodium and potassium hydroxide were also tried, but it was difficult to wash out occluded sodium and potassium nitrate, washing being continued until the filtrate gave a negative or very faint test for nitrate with diphenylamine reagent.

In a typical preparation 2 gram-molecules of copper nitrate were dissolved in 4000 cc. of warm (distilled) water, and the filtered solution was placed in a 6-gallon earthenware crock, together with an additional 8000 cc. of warm water. To this solution was added, with stirring, a warm, filtered solution of 2 gram-molecules of ammonium carbonate in 4000 cc. of water. After standing for 1 hr. the mixture was filtered by suction. The filter cake was washed on a Büchner funnel with 500 cc. of water and then returned to the crock, where it was stirred with 16,000 cc. of warm water for 15 min. After standing for 1 hr. the solution was filtered.

The chemicals used were of the highest reagent grade and their purity was checked, as well as that of the final catalyst. All utensils were washed with nitric acid and rinsed with distilled water just before use.

The precipitate was dried at 180–190°C. for 36 hr. in a porcelain dish covered with a watch glass. The dry, fluffy, black powder was pressed into a thin cake (ca. 1.5 mm. thick) in a hydraulic press with a pressure of about 2 tons per square inch. The cake was cut up with a stainless steel knife into granules ranging in size from 6 to 10 mesh. The granules were heated in a stream of nitrogen for 20 hr. at 400°C., and the resulting oxide was reduced in hydrogen.

Precipitation of pure copper from copper sulfate by hydrogen under pressure.

Pure copper was precipitated as follows: A 3515-cc. rotating autoclave of the Ipatieff type, equipped with a glass liner, was charged with 850 cc. of distilled water, 125 g. of copper sulfate pentahydrate, 4 g. of 96 per cent sulfuric acid, and 50 kg. of hydrogen per square centimeter. The bomb was rotated for 12 hr. at 150°C. The yield of metallic copper was 28.8 g. (90.5 per cent of the theoretical). The filtrate was colorless at first but became blue on standing, owing to oxidation of cuprous to cupric ion by air. The matte of sparkling, mossy copper was washed several times with water and finally with alcohol.

Reduction of copper oxide. The last step in the preparation of copper catalyst was reduction of copper oxide in a stream of hydrogen. The hydrogen purification train (figure 1) consisted of copper gauze (A) at 550°C., followed by anhydrous calcium chloride (B), Ascarite (C), and Anhydrone (D). The copper oxide (66.8 g.) was packed into a glass tube (F; 14 mm. inside diameter) and was held in place by plugs of glass wool. In case of shrinkage during reduction the catalyst was again packed by tapping. The conditions of reduction for oxide prepared from precipitated

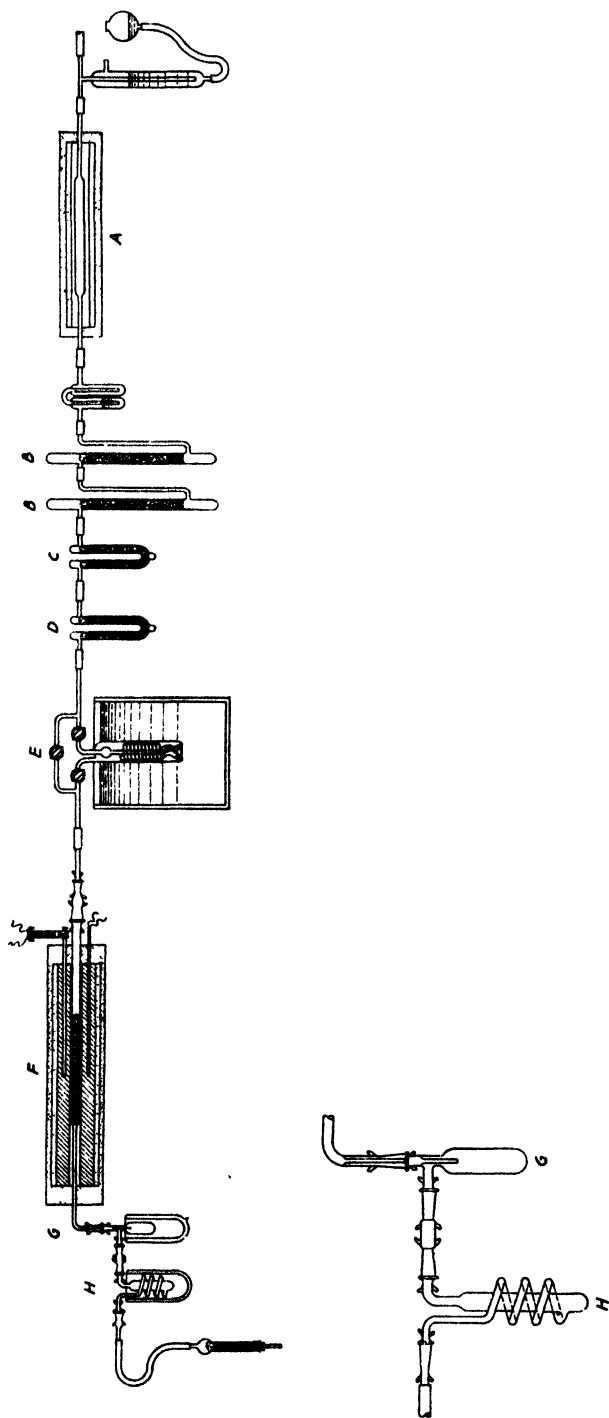


FIG. 1. Apparatus for testing activity of copper catalyst

carbonate were 20 hr. at 225°C. or 150°C., or 90 hr. at 100°C., 99.3–99.8 per cent reduction being obtained. With Kahlbaum granular oxide, which presumably had been calcined, the reduction period was 20 hr. at 225°C. The standard hydrogen rate (measured at room temperature) was 2000 cc. per hour per 66.8 g. of copper oxide. The free space of the reduced catalyst was determined after the hydrogenation run by adding water to the charged catalyst tube.

Hydrogenation test at superatmospheric pressure. Twenty grams of reduced copper and 50 cc. of benzene were charged to the glass liner of an 850-cc. rotating bomb. The glass liner was closed with a glass stopper equipped with a capillary. The bomb was rotated for 12 hr. at 350°C. under an initial hydrogen pressure of 100 kg. per square centimeter. The extent of hydrogenation was estimated from the refractive index of the liquid product.

Hydrogenation test at ordinary pressure. A mixture of benzene and 6 to 7 volumes of hydrogen was passed over the catalyst at atmospheric pressure and 225°C. The contact times used with the pure (inactive) catalysts varied from 80 to 440 sec. The activities of the impure (active) catalysts were compared on the basis of their performance at 90 sec. contact time, as found by interpolation. Four hydrogenation periods (4 to 7 hr. each, depending on the gas rate) were run with each catalyst. Repetition of the original conditions showed that the activity was constant over much longer periods of time than those used in the test. The mixture of hydrogen and benzene was obtained by bubbling hydrogen through benzene contained in a spiral wash bottle (6), the hydrogen-benzene ratio being calculated from the vapor pressure of benzene. Experiment showed that this calculation was justified, inasmuch as the ratios obtained in four experiments at 30.0°C. ranged from 5.18 to 5.35 (average 5.25), as compared with the theoretical value of 5.33.

The liquid catalysate was collected in two (sometimes three) receivers which were cooled in carbon dioxide-trichloroethylene, and sometimes the gas was also collected. The receiver system (figure 1; G and H) and the technique of handling were patterned after the description of Baxter and Hale (2). The first receiver collected about 98.9 per cent of the liquid product, the second 0.8 per cent, and the third, 0.3 per cent.

Analysis of hydrogenation product. The composition of the liquid catalysate, a mixture of benzene and cyclohexane, was determined by means of refractive index. The benzene and cyclohexane used in establishing the refractive index-composition curve were originally of c.p. quality and were further purified (15, 7, 3). The curve was plotted from the data² in table 1.

² The data of Burrows and Lucarini (4) are incorrect, owing to a typographical error as to temperature (private communication).

Method of calculation. The contact time in seconds at the temperature and pressure of hydrogenation was calculated as free space divided by gas

TABLE 1

Composition and refractive indices of benzene and cyclohexane mixtures

WEIGHT PER CENT OF		n_D^{20}
Benzene	Cyclohexane	
0.00	100.00	1.4266
20.13	79.87	1.4380
40.10	59.90	1.4510
59.78	40.22	1.4655
79.89	20.11	1.4824
100.00	0.00	1.5012

TABLE 2

Typical calculation

Hours on test	4.0
Excess pressure at inlet, inches of water	4.6
Temperature of benzene, °C	27.3
Vapor pressure of benzene at 27.3°C., mm. of Hg	105
Barometer (corrected), mm. of Hg	741
Average pressure in system, mm. of Hg	745
Hydrogen-benzene volume ratio	6.1
Liquid catalysate:	
Grams	1.200
n_D^{20}	1.4870
Weight composition, 85 per cent benzene and 15 per cent cyclohexane:	
Benzene, grams	1.02
Cyclohexane, grams	0.18
Gas volumes at 225°C. and 745 mm.:	
Benzene + cyclohexane, cc.	635
Inlet hydrogen, cc.	3870
Outlet hydrogen, cc.	3600
Average hydrogen, cc.	3735
Benzene + cyclohexane + average hydrogen, cc.	4370
Cc. of gas (225°C., 745 mm.) per second	0.304
Contact time, sec. (free space, 19.2 cc.)	63

rate per second. The gas volume was taken as the sum of the benzene and cyclohexane volumes plus the arithmetical mean of the inlet and outlet volumes of hydrogen. A typical calculation is shown in table 2.

Hydrogenation of benzene with copper catalysts

Hydrogenation at ordinary pressure and 225°C. Copper prepared by reducing Kahlbaum copper oxide (which contained 0.1 per cent of nickel) for 20 hr. at 225°C. hydrogenated benzene to the extent of 47 per cent in 90 sec. contact time.

Pure copper catalysts (table 3, Nos. 1 to 8), prepared from precipitated hydroxides and carbonates and free from other metals but containing 0.2 per cent of oxygen, showed an average hydrogenation of 1 per cent at

TABLE 3

Hydrogenation of benzene with pure copper catalysts at atmospheric pressure and 225°C.*

CATALYST NO.	PRECIPITANT	REDUCTION CONDITIONS		HYDROGENATION OF BENZENE (PER CENT) AT DIFFERENT CONTACT TIMES (C. T.)			
		Hours	T, °C.	Per cent	C. T.	Per cent	C. T.
1	NH ₄ OH	20	200	0	150	1	290
2	NH ₄ OH	20	225	0	110	0	260
3	NH ₄ OH	20	225	0	130	0	240
4	KOH	20	225	0	160	1	440
5	(NH ₄) ₂ CO ₃	90	100	0	80	2	320
6	(NH ₄) ₂ CO ₃	20	150	0	110	2	290
7	(NH ₄) ₂ CO ₃	20	200	0	110	0	240
8	(NH ₄) ₂ CO ₃	20	225	0	130	1	340
9	H ₂			0	130	0	290
10	H ₂			0	150	0	310

* Spectroscopic examination showed that these catalysts contained less than 0.005 per cent of nickel, cobalt, iron, lead, or tin, and not more than 0.01 per cent of aluminum, chromium, calcium, or magnesium. The catalysts prepared from hydroxides and carbonates showed 99.70 ± 0.05 per cent of copper by electrolysis, precautions being observed to avoid contact with air before and during weighing. Copper precipitated by hydrogen under pressure was 100.00 ± 0.05 per cent pure by electrolysis. Catalyst No. 4 contained an undetermined amount of potassium.

contact times of 240 to 440 sec. Preparations 5 and 6 were reduced at especially low temperatures (100° and 150°C., respectively) so as to guard against deactivation by heat.

Pure copper catalysts (table 3, Nos. 9 to 10), obtained in the form of large microcrystals by the reduction of copper ions by hydrogen under pressure, did not hydrogenate benzene with contact times up to 310 sec.

When clean glass beads were substituted for copper catalyst, the liquid product was unchanged benzene (with contact times of 100 to 300 sec.).

^a *Hydrogenation at superatmospheric pressure and 350°C.* Copper pre-

pared from Kahlbaum copper oxide hydrogenated benzene quantitatively in a glass-lined bomb in 12 hr. at 350°C. under an initial hydrogen pressure of 100 kg. per square centimeter.

Pure copper catalysts (table 3, Nos. 1 to 8) prepared from precipitated hydroxides and carbonates hydrogenated benzene under similar conditions to the extent of 70 to 97 per cent.

Pure copper catalysts (table 3, Nos. 9 to 10) obtained by the reduction of copper ions under pressure did not hydrogenate benzene in 12 hr. at 350°C. under an initial hydrogen pressure of 100 kg. per square centimeter.

Blank runs with benzene in the absence of copper showed that the equipment was completely non-catalytic under the conditions of the experiment.

Effect of temperature-time conditions of reduction of impure copper oxide upon hydrogenating activity of reduced catalyst. The study was made with granular (6- to 10-mesh) copper oxide (Kahlbaum-Schering, für Analyse).

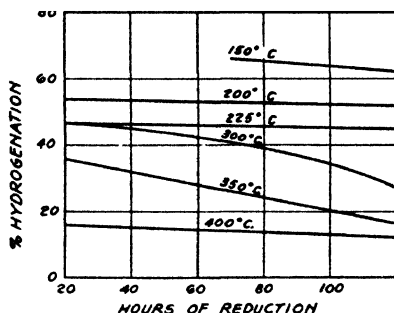


FIG. 2. Effect of temperature and time conditions of reduction on catalytic activity

The hydrogenating activity of this material was due to the presence of 0.1 per cent of nickel.

The oxide was reduced at different temperatures (150°, 200°, 225°, 300°, 350°, and 400°C.) and for different lengths of time (20 to 120 hr.). The hydrogen rate was 2000 cc. per hour (measured at room temperature), at which rate the oxide would require about 10 hr. for reduction, assuming complete utilization of the hydrogen. The amount of water produced by the reduction of 66.8 g. of oxide was 14.90 g., as compared with the theoretical value of 15.12 g. for cupric oxide. The water was collected in two receivers, one empty and ice-cooled, the other filled with Anhydrone.

The catalytic activity of the reduced catalyst was measured by its ability to hydrogenate benzene at 225°C. and ordinary pressure in a contact time of 90 sec. Figure 2 shows the effect of time and temperature of reduction upon catalytic activity.

Pease and Purdum prepared their catalyst by reducing granular copper

oxide (source not given) in hydrogen for about 50 hr. at 150°C., followed by 50 hr. at 200°C., and finally several hours at 300°C. They offered no evidence that this schedule was the optimum.

According to our experiments it is evident that low temperature of reduction (e.g., 200°C. *versus* 400°C.) favors catalytic activity, and prolonged heating (120 hr.) in hydrogen at 200° and 225°C. has little, if any, detrimental effect upon activity. On the other hand, continued heating in hydrogen at 300° and 350°C. lowers the activity decidedly, and at 400°C. the catalyst is deactivated almost as much by 20 hr. as by 120 hr. Twenty hours at 400°C. is more injurious than 120 hr. at 350°C.

Up to the present we have been unable to detect the actual physical change in the catalytic surface that is caused by the temperature and that is responsible for the loss in activity (10, 5, 1).

Effect of hydrogen rate. Activity also depends upon the hydrogen rate during reduction of the oxide. Increasing the hydrogen rate 3.5-fold decreased the activity by more than one-half. A 66.8-g. sample of Kahlbaum granular copper oxide was reduced at 225°C. (furnace block temperature) for 3 hr. in a hydrogen stream of 7000 cc. per hour (3.5 times the usual rate). The amount of water produced was 14.21 g., as compared with 14.90 g. for the usual reduction (225°C., 20 hr., 2000 cc. of hydrogen per hour). The reduced catalyst hydrogenated benzene 20 per cent, as compared with 47 per cent when the hydrogen rate during reduction of the oxide was 2000 cc. per hour. It might be expected that slow reduction with dilute hydrogen would be advantageous. However, slow reduction (67 hr. at 225°C.) with a mixture of 1 volume of hydrogen plus 3 volumes of nitrogen (combined gas rate, 2000 cc. per hour per 66.8 g. of cupric oxide) gave the same activity as reduction with hydrogen alone (2000 cc. per hour).

Irreversibility of heat deactivation. In the preparation of catalysts for heterogeneous catalysis it is important that the temperature does not exceed a certain threshold value, else the catalytic activity is lowered. The effect is irreversible. Activity is not restored by lowering the temperature. In some cases a catalyst can be reactivated by alternate oxidation and reduction, but it is not always easy, as is shown by the following examples.

Kahlbaum copper oxide (66.8 g.) was reduced at 400°C. during 20 hr., 14.16 g. of water being produced. The catalyst hydrogenated benzene 18 per cent. The catalyst was then oxidized in a stream of air. The temperature was raised from 225° to 400°C. during 4 hr. and held at 400°C. for 20 hr. The temperature was then lowered to 225°C. (in nitrogen) and the catalyst was reduced at this temperature for 20 hr., 5.46 g. of water being produced. The resulting catalyst hydrogenated benzene 22 per cent. In other words, the effect of oxidation and subsequent reduction was not decidedly beneficial.

An unsuccessful attempt was made to obtain a catalyst capable of hydrogenating benzene by alternate oxidation and reduction of copper oxide wire. This oxide wire showed a melted surface under the microscope. The copper oxide wire (Merck reagent grade) was reduced for 20 hr. in hydrogen at 225°C. and oxidized for 20 hr. in air at 400°C. About 15 per cent of the copper was oxidized in the oxidation step. Alternate oxidation and reduction was repeated six times. Care was taken that the temperature of the oxide was always lowered to 225°C. before the reduction step was started. Benzene was not hydrogenated by this material. The final catalyst contained 99.6 per cent of copper.

Temperature instability of copper catalytic surface. Low temperature is an essential factor in obtaining an active catalyst by the reduction of copper oxide; for example, 225°C. is decidedly preferable to 400°C. An obvious explanation is that the exothermic heat of the reduction reaction plus the higher initial temperature level (400°C.) is sufficient to injure the catalytic surface. But exothermicity alone cannot account for the extreme

TABLE 4

Exothermicity of copper oxide reduction at 225°C. and at 400°C.

REACTION	CALORIES PER GRAM-MOLE AT 225°C.	CALORIES PER GRAM-MOLE AT 400°C.
$\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$	+23.1	+23.4
$\text{Cu}_{225^\circ\text{C.}} \rightarrow \text{Cu}_{1083^\circ\text{C.}}$	-5.78	
$\text{Cu}_{400^\circ\text{C.}} \rightarrow \text{Cu}_{1083^\circ\text{C.}}$		-4.61

difference between the reduction temperature of 225°C. and that of 400°C., especially in view of the finding of Pease and Taylor (14) that this reduction is autocatalytic and localized at the copper-copper oxide interface. It is evident from the data presented in table 4 that the quantity of heat liberated at 225°C. is able to raise the temperature of copper to its melting point. At both temperatures there is a great excess of heat available for the destruction of catalytic surface.

Diminishing the intensity of the exothermal conditions during reduction had no effect upon the activity of the catalyst. For example, reduction of copper oxide at 400°C. with hydrogen diluted with 3 volumes of nitrogen, the combined gas rate being equal to the usual hydrogen rate (2000 cc. per hour per 66.8 g. of oxide), did not prevent destruction of the catalytic surface. Also, the same deactivation was obtained when an active catalyst (reduced at 225°C., activity 47 per cent) was heated for 10 hr. in nitrogen at 400°C. Therefore the loss of activity is primarily due to changes which take place in the temperature interval between 225° and 400°C.

Relationship between physical structure and catalytic activity

The object was to correlate the catalytic activity of copper catalyst with its physical structure. The external surface was examined microscopically, and information as to the internal structure was obtained by the emanation method.

Microscopic study. The sample of Kahlbaum granular copper oxide was a mixture of approximately 10 parts of dull granules and 1 part of granules with sparkling points. These two varieties were separated with the naked eye, and reduced and tested separately. They had the same activity, hydrogenating benzene 47 per cent at ordinary pressure and 225°C. in 90 sec. contact time. But when the oxide granules were separated under the microscope on the basis of surface porosity and the two varieties were reduced and tested separately, it was found that the compact surface type had an activity of only 8 per cent, whereas the open-work surface type had an activity of 60 per cent.

By more careful selection under the microscope it was possible to pick out granules with zero activity. On the other hand, from the commercial oxide there could be selected particles possessing an exceptionally porous surface; after reduction in hydrogen at 225°C., these particles hydrogenated benzene 90 per cent in 90 sec. contact time at 225°C. and atmospheric pressure.

When the original copper oxide mixture was reduced in hydrogen at 225°C., the reduced copper was a mixture of about equal parts of salmon-colored and reddish-brown particles. The salmon-colored particles possessed a compact burnished surface and their activity was 16 per cent. The reddish-brown particles possessed an open-work surface and their activity was 58 per cent.

In general, microscopic study of reduced copper catalysts prepared under different conditions distinguishes three types of inactive surface and one type of active surface.

Inactive surfaces. The first type is a smooth, compact, non-porous surface, without individual crystal faces. This surface (figure 3a) results from the high-temperature reduction of copper oxide, the crystal faces having melted together.

The second type is similar to the first, in that it is a compact surface without crystal faces distinguishable under the microscope. It is made up of smooth round particles (figure 3b), the melting process not having proceeded as far as with the first type. There is also another inactive surface of this second type, which is porous. X-ray examination showed the structure to consist of dispersed agglomerates of copper.

The third inactive surface is completely different from the other two. It is made up of well-formed copper crystals which measure 0.05 mm. to

0.5 mm. in length. This type of surface (figure 3c) results from the reduction of copper ions by hydrogen under pressure.

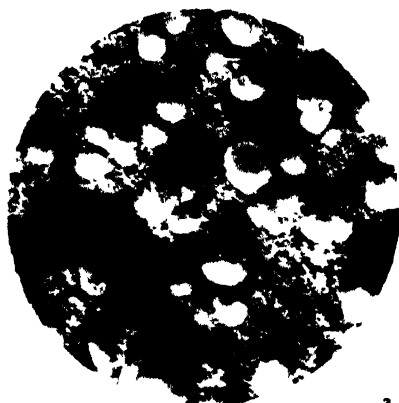
Active surface. The catalytically active surface is a spongy structure of microcrystals with many fissures between the individual crystals (figure 4). Under the microscope it resembles a loose pile of yellow crystals.



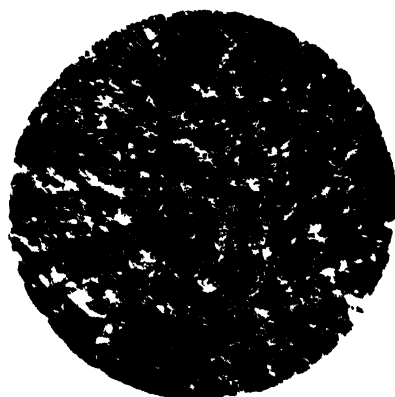
3a



3b



3c



4

FIG. 3 Inactive surfaces

FIG. 4 Catalytically active surface

Application of emanation method to determine relationship between surface and catalytic activity

During recent years the emanation method has received recognition as a tool for the measurement of the surface area of solids. This method consists in incorporating radium or radiothorium with the solid being investigated and measuring the rate of escape of emanation. Knowing the rate of escape through the individual particles, it is possible to cal-

culate the actual surface involved.³ The amount of radioactive substance was so small (10^{-9} g. of radium per gram of copper) that it had no effect upon the catalytic activity of the copper, as shown by special experiments.

Relationship between emanating power, catalyst activity, and catalyst purity

Basic copper carbonate, with and without chromium hydroxide, was precipitated in the presence of a known amount of a mixture of radium and radiothorium. Knowing the amount of radioactive material lost in the filtrate, the amount adsorbed by the precipitate was calculated. After the thorium X had come to equilibrium with the radiothorium, the rate of escape of thorium emanation was measured. The emanating power was calculated as the ratio of emanation emitted to emanation formed during unit time.

TABLE 5
Effect of 3.5 per cent of chromium oxide on emanating power

PURE COPPER			COPPER + 3.5 PER CENT OF CHROMIUM OXIDE		
<i>T</i>	Electrometer discharge,* in divisions per minute	Relative emanating power	<i>T</i>	Electrometer discharge, in divisions per minute	Relative emanating power
°C.			°C.		
27	0.32	1.0	27	12.4	38.8
200	1.72	5.4	200	13.3	41.6

* Average discharge per gram of copper over a period of 4 hr.; a constant stream of hydrogen was passed over the catalyst sample during the measurements.

One catalyst was prepared from a coprecipitate of basic copper carbonate and chromium hydroxide, the final catalyst containing 3.5 per cent of chromium oxide. The other catalyst contained no chromium oxide. Both catalysts were reduced for 20 hr. at 225°C.

The preparation containing chromium oxide catalyzed the hydrogenation of benzene to the extent of 28 per cent at 225°C. and ordinary pressure in a contact time of 90 sec., whereas that free of chromium oxide was unable to do so; the increased activity of the former was paralleled by its increased total surface as measured by its emanating power (table 5).

Relationship between emanating power and temperature

Basic copper carbonate was precipitated from a solution containing radiothorium. The precipitate was dried, decomposed, and reduced for 20 hr. at 225°C. The catalyst was then heated, cooled, and heated

This is to be discussed in a subsequent paper.

again, its emanating power being measured at the same time. It is evident from table 6 that the emanating power of this pure copper catalyst at 400°C. was only one-fourth as great in the second heating period as it was in the first.

Although the decrease in hydrogenating activity at 400°C. caused by heating is apparently paralleled by loss in surface as measured by the emanating power, a direct comparison should not be made, (1) because a pure copper catalyst is inactive initially and (2) because a temperature of 700°C. was necessary to get the above decrease in emanating power.

SUMMARY

1. The hydrogenating activities of several copper preparations have been correlated on the basis of chemical composition, conditions of reduc-

TABLE 6
Effect of temperature on emanating power of copper catalyst
(Measured in stream of hydrogen)

FIRST HEATING			SECOND HEATING		
<i>T</i>	Electrometer discharge, in divisions per minute	Relative emanating power	<i>T</i>	Electrometer discharge, in divisions per minute	Relative emanating power
°C.			°C		
25	0.13	1.0	25	0.02	0.15
225	0.54	4.2	400	0.19	1.5
325	0.70	5.4	600	0.73	5.6
400	0.84	6.5			
700	0.68	5.2			

tion, and physical structure, the latter being determined by microscopic examination and by the emanation method.

2. The hydrogenating activity of copper is very dependent upon the presence of traces of impurities, especially of nickel.

3. Copper prepared from copper oxide containing 0.1 per cent of nickel oxide readily catalyzes the hydrogenation of benzene at 225°C. and ordinary pressures.

4. Pure copper prepared from precipitated hydroxide or basic carbonate, and containing not less than 0.2 per cent of oxygen, readily catalyzes the hydrogenation of benzene at superatmospheric pressure but only slightly at atmospheric pressure.

5. Pure copper obtained by the reduction of copper ions by hydrogen under pressure and consisting of large microcrystals (0.05 to 0.5 mm.) does not catalyze the hydrogenation of benzene at atmospheric pressure or at superatmospheric pressure.

6. The presence of 3.5 per cent of chromium oxide raises the catalytic activity of copper and increases its surface as measured by the emanation method.

7. The threshold temperature at which copper catalyst rapidly loses its hydrogenating activity is 350–400°C.

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REFERENCES

- (1) ADAM, N. K.: *The Physics and Chemistry of Surfaces*, p. 286. Clarendon Press, Oxford (1938).
- (2) BAXTER AND HALE: *J. Am. Chem. Soc.* **58**, 510 (1936).
- (3) BRUUN-HICKS AND BRUUN: *J. Research Natl. Bur. Standards* **7**, 610 (1931).
- (4) BURROWS AND LUCARINI: *J. Am. Chem. Soc.* **49**, 1157 (1927).
- (5) CONSTABLE: *Proc. Roy. Soc. (London)* **113**, 254 (1926).
- (6) CORSON: *Ind. Eng. Chem., Anal. Ed.* **10**, 646 (1938).
- (7) HICKS: *J. Research Natl. Bur. Standards* **2**, 484 (1929).
- (8) IPATIEFF: *Catalytic Reactions at High Pressures and Temperatures*. The Macmillan Co., New York (1936).
- (9) IPATIEFF AND CORSON: *Ind. Eng. Chem.* **30**, 1039 (1938).
- (10) IPATIEFF AND IPATIEFF: *Ber.* **62**, 386 (1929).
- (11) IPATIEFF AND WERCHOWSKY: *Ber.* **42**, 2078 (1909).
- (12) PALMER AND CONSTABLE: *Proc. Roy. Soc. (London)* **107**, 255 (1925).
- (13) PEASE AND PURDUM: *J. Am. Chem. Soc.* **47**, 1435 (1925).
- (14) PEASE AND TAYLOR: *J. Am. Chem. Soc.* **43**, 2179 (1921).
- (15) RICHARDS AND SHIPLEY: *J. Am. Chem. Soc.* **36**, 1830 (1914).
- (16) SABATIER AND SENDERENS: *Ann. chim. phys.* [8] **4**, 368 (1905).

STUDIES ON AGING AND COPRECIPITATION. XXVII

THE COPRECIPITATION OF NITRATE WITH LEAD SULFATE AND THE DECOMPOSITION OF COPRECIPITATED NITRATE ON HEATING¹

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Several studies (2) have been carried out in this laboratory on the degree of perfection and the aging of lead sulfate obtained by precipitation of lead nitrate with potassium sulfate or by reverse precipitation. In the present study the effect of various factors, such as the concentration of the reactants, the method of precipitation, the temperature during the precipitation, and the conditions of aging, upon the amount of coprecipitated nitrate has been determined. Moreover, the effect of the heating of the air-dried precipitate upon the nitrate content of the precipitate has been determined.

EXPERIMENTAL

Determination of coprecipitated nitrate

The nitrate was reduced in alkaline medium with Devarda's alloy, and the ammonia was transferred to a wash bottle partly filled with dilute sulfuric acid.

The reduction chamber consisted of a 75-ml. Pyrex distillation flask provided with an inlet tube for air. The sample was transferred to the reduction flask, 8 ml. of a saturated sodium hydroxide solution was added and enough water to make a volume of 20 ml. Four-tenths of a gram of Devarda's alloy was then added, and a rubber stopper immediately inserted in the neck of the flask. Air washed through dilute acid and water was passed through the flask, and the ammonia was collected in a cylinder containing 40 ml. of 0.5 *N* sulfuric acid. The contents of the reduction chamber were heated gently for a few minutes at the beginning of the experiment. After 50 min. heat was again applied for a 10-min. interval to drive out the last traces of ammonia. The contents of the

¹ This article is based upon a thesis submitted by Roy A. Halversen to the Faculty of the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Master of Arts, June, 1938.

flask with 0.5 *N* sulfuric acid were transferred to a 250-ml. Erlenmeyer flask, the excess of acid was nearly neutralized with sodium hydroxide, and the ammonia was determined by the hypochlorite method of Kolthoff and Stenger (3). A blank determination was made under similar conditions, and the amount of ammonia found was subtracted from the amount

TABLE 1

Effect of concentration of reactants, method of precipitation, temperature, and conditions of aging upon coprecipitation of nitrate with lead sulfate

EXPT. NO.	CONCENTRATION OF LEAD AND OF SULFATE	TEMPERATURE OF PRECIPITATION	TEMPERATURE DURING AGING	METHOD OF PRECIPITATION	NITRATE IN PRECIPITATE AFTER AGING FOR			
					1 min.	1 hr.	6 hr.	24 hr.
	<i>M</i>	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$		per cent	per cent	per cent	per cent
1	0.4	25	25	Direct	0.61	0.46	0.33	0.27
2	0.4	25	90	Direct		0.35		0.22
3	0.4	25	25	Reverse	0.41	0.36	0.35	
4	0.1	25	25	Direct	0.64	0.42	0.29	0.20
5	0.1	25	90	Direct		0.40		0.22
6	0.1	25	25	Reverse	0.22	0.16	0.16	
7	0.1	95-100	25	Direct	0.33	0.31	0.27	0.26
8	0.1	95-100	90	Direct		0.28		0.24
9	0.1 ^(a)	25	25	Direct	0.39	0.37	0.29	0.19
10	0.1 ^(a)	25	90	Direct		0.18	0.06	0.01
11	0.1	25	25 ^(b)	Direct		0.38	0.25	0.16
12	0.1	25	90 ^(b)	Direct		0.12	0.04	0.01
13	0.1 ^(c)	25	25	Direct	0.28	0.31	0.32	0.30
14	0.1 ^(c)	25	90	Direct		0.34		0.31
15	0.1 ^(c)	25	25	Reverse	0.30		0.26	
16	0.1 ^(c)	25	25 ^(d)	Direct				0.20
17	0.1 ^(c)	25	90 ^(d)	Direct				0.05
18	0.025	25	25	Direct	0.55	0.50	0.44	0.44
19	0.025	25	90	Direct		0.43		0.32
20	0.025	25	25	Reverse	0.19	0.16	0.14	
21	0.025 ^(e)	25	25	Direct	0.53		0.62	
22	0.025	25	25 ^(f)	Direct			0.22	0.14
23	0.025	25	90 ^(f)	Direct				0.09

(a) Lead nitrate solution was 0.01 *N* in nitric acid; (b) supernatant liquid was made 0.01 *N* in nitric acid; (c) lead nitrate and potassium sulfate in 15 per cent ethanol; (d) precipitate was filtered and aged in 0.1 *N* nitric acid; (e) lead nitrate solution was 0.5 *N* in potassium nitrate; (f) precipitate was filtered and aged in 0.5 *N* nitric acid.

found in the unknown. Working with 1 mg. of nitrate and subtracting the blank yielded results varying between 0.995 and 1.00 mg. in ten experiments.

In the determination of coprecipitated nitrate in lead sulfate it was not found necessary to decompose the precipitate first by boiling with sodium

carbonate solution; the same results were found by the above procedure as after boiling with the carbonate solution.

Methods of precipitation

Direct method (sulfate added to lead): (1) 0.4 *M* solutions: 2.447 ml. of 0.4 *M* potassium sulfate added to 2.567 ml. of 0.4 *M* lead nitrate. (2) 0.1 *M* solutions: 9.79 ml. of 0.1 *M* potassium sulfate added to 10.27 ml. of 0.1 *M* lead nitrate. (3) 0.025 *M* solutions: 39.16 ml. of 0.025 *M* potassium sulfate added to 41.08 ml. of 0.025 *M* lead nitrate. The time of precipitation in all cases was 20 to 30 sec. The precipitations were carried out at room temperature in most cases, but at boiling temperature in some cases (see table 1). Several experiments have been carried out

TABLE 2

Direct precipitation

Ten ml. of 0.1 *M* potassium sulfate was added to 10 ml. of 0.15, 0.3, or 0.5 *M* lead nitrate

CONCENTRATION OF LEAD NITRATE	TEMPERATURE OF PRECIPITATION	TEMPERATURE OF AGING	NITRATE IN PRECIPITATE AFTER AGING FOR			
			1 min.	1 hr.	6 hr.	24 hr.
<i>M</i>	°C.	°C.	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
0.15	25	25	0.43	0.40	0.37	0.36
0.15	95	25	0.32	0.25	0.22	0.21
0.30	25	25	0.34	0.30	0.30	0.29
0.30	95	25	0.27	0.26	0.24	0.23
0.30	25	90*				0.09
0.50	25	25	0.36	0.34	0.32	0.34
0.50	95	25	0.32	0.29	0.26	0.34
0.50	25	25*				0.11

* Aged in 0.01 *N* nitric acid.

in which 0.1 *M* potassium sulfate was added to a large excess of a stronger lead nitrate solution (table 2).

Method of reverse precipitation. The lead nitrate solution was added to the potassium sulfate solution. The ratio of lead to sulfate was the same as in the direct precipitations. For the determination of nitrate in the fresh precipitates the latter were filtered immediately and washed with six successive 5-ml. portions of conductivity water. After drying, weighed portions were transferred to the reduction flask. (The time required for filtration and washing was 5 to 6 min.)

When the precipitates were aged they were placed with the supernatant liquid on a shaker (400 rotations per minute) at room temperature or digested at 90°C. Unless stated otherwise, the aging occurred in the

supernatant liquids. After aging the precipitates were washed, etc., as described above.

The results are expressed in per cent of nitrate in the precipitates.

Experimental results

A condensed summary of a great number of experiments is given in table 1. In table 2 a few of the results are reported in which the 0.1 molar sulfate solution was added to a large excess of lead nitrate. All the figures reported are the average of at least three independent experiments.

It was of interest to know whether all of the coprecipitated nitrate was occluded or if part was adsorbed on the active surface of the precipitate. It is to be expected that adsorbed lead nitrate would be easily removed upon treatment with a slight excess of sulfate. Upon addition of 9.79 ml. of 0.1 *M* potassium sulfate to 10 ml. of 0.1 *M* lead nitrate at room temperature the fresh precipitate contained 0.64 per cent of coprecipitated nitrate. When 10.27 ml. of 0.1 *M* sulfate was added to the nitrate solution instead of 9.79 ml. the fresh precipitate contained 0.40 per cent of coprecipitated nitrate. This amount of coprecipitated nitrate decreased very slowly upon aging at room temperature in the supernatant liquid (0.34 per cent after 24 hr.). These experiments would indicate that, in the presence of a slight excess of lead nitrate in the supernatant liquid, $0.64 - 0.40 = 0.24$ per cent of the coprecipitated nitrate, or about 35 per cent of the total amount, is adsorbed on the active surface. This conclusion was substantiated by the following experiments: Equivalent amounts of 0.1 *M* sulfate and lead nitrate were mixed (direct precipitation); the fresh precipitate contained 0.59 per cent of coprecipitated nitrate. When 0.5–1 ml. of 0.1 *M* potassium sulfate was added 15 sec. after the precipitation the amount of coprecipitated nitrate was 0.46 per cent, while this amount was equal to 0.64 per cent when a slight excess of lead was added after the precipitation. These experiments would indicate that about 30 per cent of the coprecipitated nitrate is adsorbed on the active surface.

Thermal aging in the dry state

The progress of perfection and the change of the specific surface of fresh air-dried lead sulfate prepared from 0.1 *M* solutions has been studied by Kolthoff and Rosenblum (2, e). In the following experiments 30 g. of a similar product was prepared; it was immediately washed four times with 100-ml. portions of water, and air-dried. Samples of 300 mg. were placed in a furnace and heated for 24 hr. at 100°, 200°, 300°, 400°, and 500°C., respectively. After cooling, the samples were washed six times with 5-ml. portions of water. The nitrate contents of the collected washings and of the washed precipitate were then determined. The original air-dried product contained 0.71 per cent of coprecipitated nitrate; after washing

six times with the 5-ml. portions of water 0.50 per cent of nitrate was found in the precipitate and 0.21 per cent (referred to the original precipitate) in the combined washings. A second series of washings yielded only 0.03 per cent of the nitrate in the combined filtrates (30 ml.); a third washing 0.01 per cent. Apparently, in the first six washings mainly adsorbed nitrate is removed; upon further washing a trace of occluded nitrate enters the liquid as a result of recrystallization. The results of the heating experiments are given in table 3.

DISCUSSION OF RESULTS AND CONCLUSIONS

From table 1 it is evident that, when equimolecular solutions of lead nitrate and potassium sulfate with concentrations varying between 0.4 and 0.025 *M* are mixed at room temperature (direct precipitation), the amount of coprecipitated nitrate is of the same order of magnitude (0.5 to 0.6 per cent). When the sulfate solution (0.1 *M*) is added to a large excess

TABLE 3

Nitrate content of precipitate and first set of washings after heating for 24 hr. at 100–500°C.

TEMPERATURE OF HEATING	NITRATE IN WASHED PRECIPITATE	NITRATE IN WASHINGS (PER CENT OF PRECIPITATE)	TOTAL NITRATE IN HEATED PRECIPITATE
°C.	per cent	per cent	per cent
100	0.50	0.21	0.71
200	0.50	0.21	0.71
300	0.50	0.17	0.67
400	0.31	0.04	0.35
500	0.01	0.0	0.01

of lead nitrate (0.15 to 0.5 *M*, table 2), the amount of coprecipitated nitrate is smaller (0.3 to 0.4 per cent). Upon direct precipitation of lead sulfate from 0.1 *M* sulfate and lead nitrate solutions prepared in 15 per cent ethanol, the amount of coprecipitated nitrate is smaller than when aqueous solutions are mixed.

When the precipitate is formed at 95–100°C. the amount of coprecipitated nitrate is smaller than when the precipitate is formed at room temperature. Addition of a little nitric acid to the lead nitrate solution results in a decrease of the coprecipitated lead nitrate (experiments 9 and 10 in table 1). Apparently part of the nitrate is coprecipitated as basic salt, and the coprecipitation of nitrate in this form is probably prevented by the acid. Addition of 0.5 *M* potassium nitrate to the 0.025 *M* lead nitrate solution had no effect upon the amount of coprecipitated nitrate (experiment 21, table 1). Evidently the nitrate is coprecipitated as lead nitrate and not in the form of potassium nitrate.

In agreement with the rules of coprecipitation (1) it is found that by reverse precipitation less nitrate is obtained in the precipitate than by direct precipitation.

Upon aging of the precipitate the amount of coprecipitated nitrate decreases. The speed of purification of the precipitate upon aging depends upon the degree of perfection of the fresh precipitate and upon the solubility of the precipitate in the aging medium. The precipitates obtained from 0.025 *M* solutions (table 1) are more perfect than those obtained from more concentrated solutions; consequently the amount of coprecipitated nitrate in the former decreases much less upon aging at room temperature and at 90°C. than in the latter (compare, e.g., experiments 18 and 19 with experiments 1, 2, 4, and 5 in table 1). When the solubility of the lead sulfate in the aging medium is very small, as is the case in the experiments in table 2 when the aging medium contained a large excess of lead, very little purification (recrystallization) occurs on aging. The same is true for the precipitates prepared and aged in 15 per cent ethanol (experiments 13 to 17, table 1).

On the other hand, when the solubility of the precipitate in the aging medium is increased by the addition of nitric acid, a drastic perfection and purification occurs, particularly at 90°C., as is evidenced from experiments 9, 10, 11, 12, 16, 17, 22, and 23 in table 1 and the last experiment in table 2. Even the fairly perfect precipitate obtained from 0.025 *M* solutions loses the greatest part of the coprecipitated nitrate upon aging in 0.5 *N* nitric acid. From an analytical viewpoint it is of great interest that an impure precipitate obtained from 0.1 *M* solutions becomes free of nitrate when aged for 24 hr. at 90°C. in 0.01 *N* nitric acid.

The precipitate formed by direct precipitation of 0.1 *M* solutions at room temperature contains about 30 per cent of the coprecipitated nitrate adsorbed on the active surface when the supernatant liquid contains an excess of lead. During the aging and perfection the active surface decreases rapidly; the initial decrease of the amount of coprecipitated nitrate on aging is, therefore, mainly due to a decrease of the active surface. Lead nitrate when exposed to the air decomposes at 233°C. It is evident from table 3 that occluded nitrate in lead sulfate does not decompose, and the adsorbed nitrate decomposes only very slightly at 300°C. After heating for 24 hr. at 400°C. practically all of the adsorbed nitrate is decomposed and only a small fraction of the occluded nitrate. After heating for 24 hr. at 500°C. all of the coprecipitated nitrate is decomposed.

SUMMARY

1. The effect of conditions of precipitation, of concentration of the reactants (lead nitrate and potassium sulfate), and of aging under varying conditions upon the coprecipitation of nitrate with lead sulfate has been determined.

2. Of analytical interest is the fact that after aging for 24 hr. in dilute nitric acid at 90°C. practically all of the coprecipitated nitrate is eliminated from the precipitate.

3. Evidence is given that about one-third of the nitrate coprecipitated with lead sulfate formed at room temperature by direct precipitation of 0.1 *M* lead nitrate with 0.1 *M* potassium sulfate is adsorbed on the active surface. This adsorbed nitrate decomposes when the precipitate is heated for 24 hr. at 400°C., while only a small fraction of the occluded nitrate decomposes at this temperature. At 500°C. all of the occluded nitrate decomposes after 24 hr. of heating.

REFERENCES

- (1) KOLTHOFF, I. M.: J. Phys. Chem. **36**, 860 (1932).
- (2) KOLTHOFF, I. M., AND ROSENBLUM, CH.: (a) J. Am. Chem. Soc. **56**, 1264 (1934); (b) J. Am. Chem. Soc. **56**, 1858 (1934); (c) J. Am. Chem. Soc. **57**, 597 (1935); (d) J. Am. Chem. Soc. **57**, 607 (1935); (e) J. Am. Chem. Soc. **57**, 2573 (1935); (f) J. Am. Chem. Soc. **57**, 2577 (1935); (g) J. Am. Chem. Soc. **58**, 116 (1936); (h) J. Am. Chem. Soc. **58**, 121 (1936).
- (3) KOLTHOFF, I. M., AND STENGER, V. A.: Ind. Eng. Chem., Anal. Ed. **7**, 79 (1935).

OCTAHEDRAL ARSENIOS OXIDE

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The present study relates to octahedral arsenious oxide free from traces of the monoclinic variety and free from arsenic in the pentavalent form. There are two familiar crystalline forms (monoclinic and octahedral),—a metastable γ crystalline form reported by Smits and Beljaars (2, 11), and a glassy form which is supposedly the solid supercooled liquid. The octahedral form is the stable form at room temperature. Bussy (3) and Winkler (13) have shown that the glassy form when dissolved in water recrystallizes as the octahedral form.

HOMOGENEITY OF CRYSTAL FORM

Both octahedral and monoclinic crystals may appear needle-like. Broken and fragmentary crystals are apt to be confused visually when the particles are small. However, only the monoclinic form shows birefringence. The extinction of polarized light by the crystals when viewed with a petrographic microscope allows easy detection of the presence of the monoclinic form.

PURIFICATION BY RECRYSTALLIZATION FROM HYDROCHLORIC ACID

Hydrochloric acid is strongly adsorbed on crystals obtained by recrystallization of arsenious oxide from hydrochloric acid. Kolthoff (7) recommends recrystallization from water until the filtrate is no longer acid to dimethyl yellow.

Results of gravimetric determinations of chloride made on several samples of arsenious oxide recrystallized from hydrochloric acid, according to directions by Anderson and Story (1), are given in table 1. The purest arsenious oxide, purified by taking central cuts of repeated sublimations, was used as a control in the gravimetric procedure. Chloride found in this blank (0.015 per cent, probably due to the reagents) was subtracted from the other determinations. The solutions of the arsenious oxide from hydrochloric acid had an approximate pH of 4.

The adsorption of water by solid glassy arsenious oxide has been re-

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ported by Krüger (8) and Winkler (13). In attempting analyses to 0.01 per cent it was evident that even the purest octahedral form showed some tendency to adsorb moisture. Commercial c.p. arsenious oxide and octahedral arsenious oxide prepared according to the method of Anderson and Story were more hygroscopic than the purer materials. All samples were dried at 105–110°C. for at least 5 hr. and cooled in a desiccator before analysis. The purest resublimed arsenious oxide was taken as a standard. The iodimetric determinations of arsenious oxide given in the last column of table 1 showed that the principal impurity was chloride.

MOLECULAR DISTILLATION

A satisfactory apparatus for efficient purification by sublimation or molecular distillation must allow: (a) distillation in the absence of air; (b) removal of the first part of the sublimate to eliminate impurities

TABLE 1
Octahedral arsenious oxide recrystallized from hydrochloric acid

SAMPLE	PREPARATION	HCl (GRAVIMETRIC)	As ₂ O ₃ (IODIMETRIC)
		per cent	per cent
1	Method of Anderson and Story	0.0540	99.940 ± 0.02
2	Method of Anderson and Story	0.0520	
3	Method of Anderson and Story; washed eight times with boiling water.	0.0189	99.978 ± 0.02
4	Commercial c.p.		99.785 ± 0.03
5	Purest sublimed (this investigation)	0.0	100.00

boiling or subliming at low temperatures; and (c) separation of the sublimate residue or high-temperature impurities.

The molecular still shown in figure 1, made entirely of Pyrex glass, fulfilled these requirements. The outside tube, B, was about 5 cm. in diameter and 30 cm. long, with a ground-glass joint, A, at the top. Near the top, just below the ground joint, there was a side tube, C, which was connected by heavy rubber tubing through a liquid-air trap to a mercury vapor diffusion pump backed by a Nelson vacuum pump. The male part of the ground joint was made as a removable condenser. It narrowed rapidly to a tube D, 2.5 cm. in diameter and flat at the lower end. This left a clearance of less than 1 cm. between the condenser and the side walls and of 4 cm. at the bottom. The incoming cooling water was led through a central tube, E, to the flat end surface on which the sublimate collected, and the cooling water outlet, H, was in the top of the condenser.

The still was heated in an electric furnace, F, with a conical bottom and cylindrical side walls 15 cm. high. The bottom and side wall windings

of the furnace were connected in parallel, and the temperature was controlled with an outside rheostat. The ground joint, lightly greased at the upper edge only, was 15 cm. above the top of a conical asbestos shield, G, which was fitted tightly around the still at the top of the furnace. Liquid air, or a mixture of cracked ice and salt, was used in an interchangeable low-temperature condenser, I, consisting of an open-mouth condenser tube supported by the ground joint and extending 10 cm. above it to protect it from the large temperature gradient.

Temperatures in the furnace were measured by a mercury thermometer against the still at the bottom. The temperatures and temperature

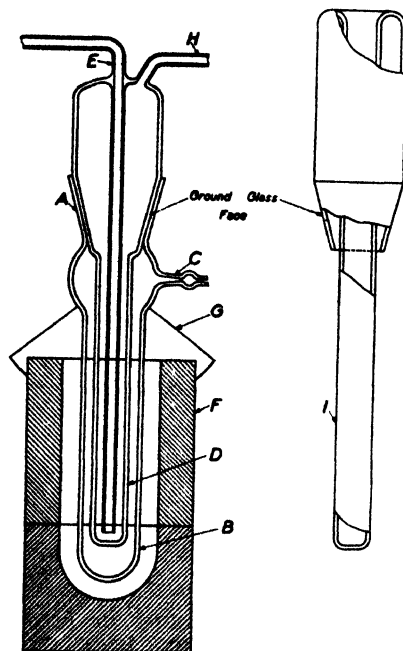


Fig. 1. Molecular still for sublimation of arsenious oxide

gradients within the still were not measured, but the temperature control was flexible and reproducible. The pressure in the outlet line as measured by a McLeod gauge was about 10^{-5} mm. of mercury. It was roughly estimated that, at 150° C. and at a pressure of 10^{-3} mm. of mercury, the mean free path of vaporized arsenious oxide molecules is of the order of magnitude of the distance from the bottom of the still to the condenser.

Removing the central condensing unit always shook part of the impure sublimate back into the material in the still, thus decreasing the efficiency of purification. This necessitated repeated sublimations of the impurities that volatilized at a low temperature.

Kahlbaum's "Arsenige Säure glasig zur Analyse" was ground to particles of 20 mesh or finer, and 30 to 40 g. of it were put in the still. The still was evacuated, and the temperature was then raised to 125°C. and held there for at least 2 hr. Pumping was continued throughout the sublimation process. The temperature was then raised to and maintained at 200°C. for 3 to 6 hr., or until a good coating of sublimate was formed at the bottom of the condenser. As reported by Smits and Beljaars (11), the first material to sublime was a reddish solid.

The furnace was lowered, the still allowed to cool to room temperature, the vacuum broken, the condenser unit taken out, and the reddish solid removed. The condenser unit was then replaced, the vacuum applied, and sublimation continued as before. With each repetition of the process the material collected on the condenser became lighter in color until it was pure white (four to six repetitions). Sublimate fractions were removed at least twice after the material collecting on the condenser had become pure white.

The temperature of the sublimation was now raised to 235°C., where practically all the oxide formed in a cake on the end of the condenser in 4 to 6 hr. The still was cooled, and the residue discarded. The cake was ground and resublimed three or four times, although there was no real impurity evident after the first sublimation. The arsenious oxide cake was a mixture of true and distorted octahedral crystals. It was used for the standardization of iodine solutions and for the preparation of octahedral crystals of true form.

SUBLIMATION IN EVACUATED TUBES

Welsh and Duschak (12) obtained octahedral crystals of true form by very slow sublimation of arsenious oxide in evacuated flasks. A flask containing the solid was set on a group of electric lamps, and a small crop of octahedral crystals was obtained in 1 month. We sought to increase the rate of formation by sublimation at a higher temperature. About 30 g. of the above pure arsenious oxide was put into a Pyrex tube, 7 cm. in diameter and drawn down to a narrow neck to facilitate sealing. The tube was baked at 130°C. while it was evacuated with a mercury diffusion pump and sealed.

The half of the evacuated tube (E, figure 2) containing the solid was placed in the electric furnace, A, at 235°C., where it was centered by blocks of diatomaceous brick, B. The part of the tube outside the furnace was protected from furnace radiation by the tight-fitting asbestos shield, C. This whole system was put in an electric oven. A ring of air jets, D, blowing onto the tube sharpened the temperature gradient between furnace and oven.

With the cool part of the tube at room temperature true and distorted

octahedral crystals were obtained; at 100°C. the percentage of true octahedra in the mixture of crystals was increased; at 170–180°C. the first crystals appeared to be true octahedra. As the crop of crystals increased, the octahedra, from the furnace outward, were progressively transformed by heat from the furnace into needles, which were later found to be distorted octahedra or chains of small octahedra having a needle-like appearance. No birefringence was shown, so there were no monoclinic crystals. Jets of air blown directly onto the tube did not stop this change in form.

Another evacuated tube containing arsenic trioxide was laid directly on the asbestos cover of the heating element (temperature = 125–130°C.) of a 100°C. electric oven. Sublimation was extremely slow, but a good crop of octahedral crystals was obtained in about 3 weeks. Here again the

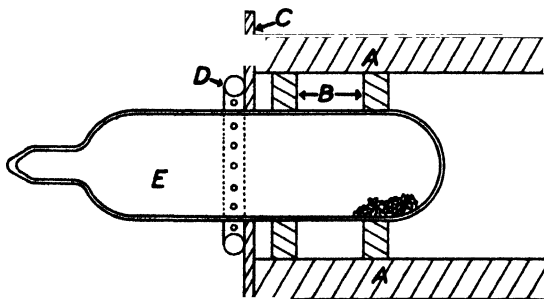


FIG. 2. Sublimation of arsenious oxide in sealed evacuated tube

crystals on the sides of the tube nearer to the source of heat slowly became transformed into the needle-like octahedral forms.

CRYSTALLIZATION FROM HOT WATER

Chapin (4) purified arsenious oxide by discarding the first fractions crystallized from hot water. He considered his product very pure, but always found a slight darkening on resublimation. Following his directions 150 g. of pure arsenious oxide which had been resublimed several times (above preparation) were made into a cream with a little water and added to 2 liters of boiling distilled water in a 3-liter boiling flask. The mixture was boiled for about 1½ hr. or until the volume was reduced to 1600 ml., and allowed to settle for a few minutes. The solution was then filtered through a cotton plug filter and cooled in cracked ice. The crystals were pure octahedra. Antimony was found to be absent.

It seemed certain that some of the pentavalent form would be formed by air oxidation in Chapin's procedure, so all operations were done under nitrogen. The water was first boiled while nitrogen was bubbled through

to remove dissolved oxygen. A strong stream of nitrogen was passed through the solution during the long boiling period, and the solution was filtered and transferred to the nitrogen-filled crystallizing flask by means of a pressure of nitrogen.

About 40 g. of these octahedral crystals were sublimed in themolecular still at 235°C. All arsenious oxide was sublimed out of the mixture by repeated sublimation. The residue, which was mostly organic matter (probably from the rubber stoppers and tubing used in handling the large quantities of boiling solutions in an atmosphere of nitrogen), was bulky but light and weighed 0.0129 g. It was analyzed and showed 0.855 per cent of the residue to be arsenic pentoxide, i.e., 0.000275 per cent of the octahedral crystals was arsenic pentoxide.

This amount of impurity seems of no consequence; however, even this trace of arsenic pentoxide introduces an appreciable error in the pH of saturated solutions of arsenic trioxide.

SINGLE OCTAHEDRAL (GLASSY) CRYSTALS

About 15 g. of octahedral crystals from the recrystallization from hot water were put in a tube 2 cm. in diameter and 15 cm. long. This was well evacuated and sealed. It was put in the center of a tubular electric tube furnace 2.5 cm. by 45 cm., with the ends closed, and heated to 195–200°C. (m.p., 272.1°C.(2)) for 3 days, and then allowed to cool.

All the arsenious oxide had distilled to one end of the tube, where the furnace must have been slightly cooler, and had formed a solid mass of perfectly clear glassy material, although no formation of glass had been expected at this temperature. The glass when broken showed planes of fracture identical with those of octahedral crystals, and had the same index of refraction as the octahedral form. The clear glass was evidently a single crystal of octahedral arsenious oxide.

CRYSTAL FORMS FROM THE MOLECULAR STILL

Tinted crystals

The first lots of octahedral crystals formed by resublimation of the product from the hot water crystallization had a purple tint, and a sooty residue was left in the still. Sublimation at a low temperature, 220°C., first separated a sooty deposit on the condenser. This low-temperature treatment was repeated until the deposit on the condenser was no longer dark. The bulk of the material was then sublimed, requiring 8 to 12 hr. at 220°C., and the sooty residue was removed. This process was repeated until two successive sublimations showed no dark, low-temperature volatile matter and no sooty residue. This purification required from four to six sublimations, but the pure crystals had no color.

Planar structure of the octahedral form

With a poor vacuum in the molecular still and the furnace at 220°C. sublimation was extraordinarily slow. At the end of 6 hr. only a few short needle-like crystals and a few plates about 1 cm. on a side had grown from the condenser into space. The crystal angles and index of refraction of the plates were those of octahedral arsenious oxide. The small octahedra had grown face-on-face, forming a planar structure.

Needle-like octahedral crystals

A needle-like crystal of octahedral arsenious oxide was first described by Gaenge (6), who cast doubt on the formation of the needle-like monoclinic crystals prepared by Debray (5) and previous investigators.

The needle-like crystals produced in the slow heating of well-formed octahedral crystals, or in the mixture of crystals formed in too rapid sublimation (probably also due to overheating), were of two types. One needle-like form was made up of chains of small octahedra, as described by Gaenge. The corners of the octahedra were rounded (figure 3a), showing an evident softening of the crystal. The other form of crystal (figure 3b) is composed of octahedra so distorted in form that they are needle-like. The crystals show four-sided peaks, and a tendency to be octahedral with the plane faces warped to form long figures. Neither of the needle-like forms of octahedral crystals shows the birefringence of the monoclinic form. Both indicate a softening of the crystal to a semifluid state, which was produced at temperatures as low as 130°C. over a long heating period. Masses of the needle-like octahedral crystals 3 to 4 cm. in length were produced in the molecular still at 260°C. with a nitrogen pressure of 10 cm., which cut down the mean free path of the arsenious oxide molecules so that there was no sublimation to the condenser.

The softening of octahedral crystals was observed by Welsh and Duschak (12) at 254°C. They thought that this was the melting point of the octahedral form.

The observation of the glassy octahedral masses which we have made, and the interpretation of the distorted microscopic octahedra as an intermediate form between the definitely octahedral and the glassy octahedral form, permit of a new interpretation of the vapor pressure data of Smits and Beljaars (11), Welsh and Duschak (12), Rushton and Daniels (10), and Niederschulte (9). All reported vapor pressure determinations show liquid arsenious oxide, for which the $\log P$ versus $1/T$ plot was a straight-line continuation of the vapor pressure curve of the octahedral form. This must be interpreted as showing no heat of transition between the crystalline octahedral arsenious oxide and the viscous liquid form. We propose that previous investigators observed a form which we may call "octahedral liquid" arsenious oxide. Beljaars (2) observed a vapor

pressure of liquid arsenious oxide which gave a straight-line $\log P$ versus $1/T$ curve intersecting the octahedral curve at 272.1°C . (melting point)



FIG. 3. (a) Distorted softened needle-like chain of octahedral crystals of arsenious oxide. (b) Distorted needle-like octahedral crystals of arsenious oxide. (Magnification $\times 80$.)

at 0.0344 atm. and corresponding to a heat of transition of 15,099 cal. per mole. He also observed a unidirectional transition, as indicated by

a log P versus $1/T$ curve, of the "octahedral liquid" into ordinary liquid; this transition became complete on superheating to about 300°C., depending on the time allowed.

True octahedral crystals

The operating conditions of the molecular still were studied to produce well-formed octahedral crystals. The results are summarized in table 2.

TABLE 2
Operating conditions of the molecular still

TEMPERATURE		PRESSURE	CRYSTALS
Furnace	Condenser		
°C.	°C.		
235	20	Good vacuum	Octahedra; distorted octahedra where material on condenser had grown toward side wall of still
235	-15	Good vacuum	Octahedra; distorted octahedra where material on condenser had grown toward side wall of still
235	-190	Good vacuum	More distorted octahedra; few monoclinic in first layer of sublimate on condenser
230	-190		
260	-190		
300	20	Good vacuum	True well-formed octahedra
330	20	Good vacuum	
380	20	Good vacuum	
			(Distorted octahedra, glassy shards, produced on prolonged heating)
230	20	Poor vacuum	Small sublimate of a few needles and plates of octahedra
260	20	0.13 atm. of nitrogen	No sublimate; needles and distorted octahedra; few monoclinic in fused material on still wall

Operation of the still at 300°C. with a water-cooled condenser gave crystals of true octahedra, some of which were as large as 3 mm. on a side, and 30 to 40 g. of arsenious oxide were sublimed in 3 or 4 hr. Rapid and efficient sublimation, with no long heating period to allow the transition into a semi-glassy form, gave true well-formed octahedra in each case.

A few monoclinic crystals were always found in the partially fused material collecting on the still walls at temperatures of 260°C. or above. If the

sublimate was collected on the condenser cooled by liquid air, a few monoclinic crystals were always found in the first layer of sublimate.

SUMMARY

Arsenious oxide recrystallized from hydrochloric acid could not be washed free from chloride.

Recrystallization of arsenious oxide from boiling water produced traces of the arsenic oxide.

The vacuum molecular still described gave very efficient purification of arsenious oxide by sublimation.

Conditions in the operation of the molecular still were found which gave a sublimate of true well-formed octahedral crystals.

Arsenious oxide crystals of needle-like appearance which do not show the birefringence of the monoclinic form were prepared. They were composed of chains and distorted octahedra indicating partial fusion. This form is believed to be closely related to an "octahedral liquid" derivable from the octahedral form with a small heat of transition.

We wish to express our thanks for the assistance of Professors A. Pabst and C. A. Anderson of the Department of Geology, University of California (at Berkeley), in the identification of the crystal forms.

REFERENCES

- (1) ANDERSON AND STORY: *J. Am. Chem. Soc.* **45**, 1102 (1923).
- (2) BELJAARS: *Proefschrift*, Amsterdam, 1931.
- (3) BUSSY: *Compt. rend.* **24**, 774 (1847).
- (4) CHAPIN: *Ind. Eng. Chem.* **10**, 522 (1918).
- (5) DEBRAY: *Bull. soc. chim.* **2**, 9 (1864).
- (6) GAENGE: *Sitzber. Jena Ges. Med. Naturwissenschaften* **1878**, ii (1879); *Jahrb. Mineral. Geol. Palaeo.*, p. 621 (1879).
- (7) KOLTHOFF: *Die Massanalyse*, p. 349. Julius Springer, Berlin (1927).
- (8) KRÜGER: *Arch. ges. Naturl. (Kastner)* **2**, 473 (1824).
- (9) NIEDERSCHULTE: *Dissertation*, Erlangen, 1903.
- (10) RUSSETON AND DANIELS: *J. Am. Chem. Soc.* **48**, 384 (1926).
- (11) SMITS AND BELJAARS: *Proc. Acad. Sci. Amsterdam* **34**, 1141, 1318 (1931); *Z. physik. Chem.* **A167**, 273 (1933).
- (12) WELSH AND DUSCHAK: *U. S. Bur. Mines, Tech. Paper No. 81* (March, 1915).
- (13) WINKLER: *J. prakt. Chem.* **139**, 247 (1885).

SPECIFIC EFFECTS OF CERTAIN TISSUE EXTRACTS ON THE CRYSTALLIZATION PATTERN OF CUPRIC CHLORIDE

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Numerous investigators have noticed that the pattern in which salts crystallize from solution is influenced by the presence of impurities. Ord (13) noted this effect particularly in connection with the growth of concretions in the body. Marriage (11) showed that adulterants in commercial jams and jellies could be detected by the size and arrangement of lead iodide crystals grown in them. Alexander (5) speaks of the effect of traces of foreign matter on the tensile strength of metals, and repeatedly mentions (1, 2, 3, 4, 6, 7) the effects of colloids on crystallization. du Noüy (9) found that a trace of adsorbable matter influenced the crystallization of sodium chloride, and that normal serum gave different results from immune sera (10). Michaud (12) has described some amusing results in the production of crystalline arborescences with urea in the presence of various colloids.

Except for the work of Marriage, Michaud, and possibly that of du Noüy, there is little in these references to indicate that a given colloid may produce a characteristic effect. Pfeiffer (14, 15, 16) found that cupric chloride crystals formed characteristic patterns if they crystallized from solutions that contained extracts of living tissues. This work has been criticized because it starts with a full-fledged hypothesis which is by no means confirmed by his experimental work. Trumpp and Rascher (17) have applied Pfeiffer's methods in an attempt to determine the presence of specific hormones in urine as a possible method for the diagnosis of pregnancy. Their success was about the same with this as with other methods based on the detection of hormones.

The present paper is an attempt to clarify some of Pfeiffer's work and to extend it. The methods are, in general, modifications of Pfeiffer's.

METHODS

The crystallization dishes are circular glass plates, each provided with a rim of Pyralin 10 cm. in diameter. The rim is applied by wrapping a strip of Pyralin $12\frac{1}{2}$ in. x $\frac{3}{8}$ in. x 0.015 in. around a petri dish, gluing it to the carefully cleaned glass plate with a 10 per cent solution of Pyralin in acetone, and removing the petri dish.

A stock solution of cupric chloride is prepared by dissolving 250 g. of the salt in water and diluting to 1 liter. This is boiled with activated charcoal and filtered; if a faint turbidity due to cupric hydroxide appears, a very little hydrochloric acid is added.

For crystallization 2 cc. of the stock solution is placed in a test tube, the solution to be tested is added, and the volume is brought to 8 cc. with distilled water. The solution is mixed thoroughly by pouring it back and forth from one test tube to another; it is then poured into one of the crystallizing dishes on a level table and allowed to evaporate spontaneously.

It is important that the temperature be constant (27–30°C.) during evaporation, that the air be entirely free from draughts, and that the relative humidity be below 60 per cent. These conditions have been obtained by the use of an entirely enclosed and insulated cabinet 4 ft. x 4 ft. x 5 ft. or larger, with the temperature thermostatically controlled and with trays of crude calcium chloride present to absorb water. Satisfactory results have never been achieved in a space smaller than that mentioned, or in a room with windows in it. Evaporation may take from 8 to 14 hr.

Under these conditions, when the cupric chloride solution alone is used a "blank" plate results, *viz.*, irregular heaps of crystals scattered over the plate, often leaving patches of clear glass (see figure 10).

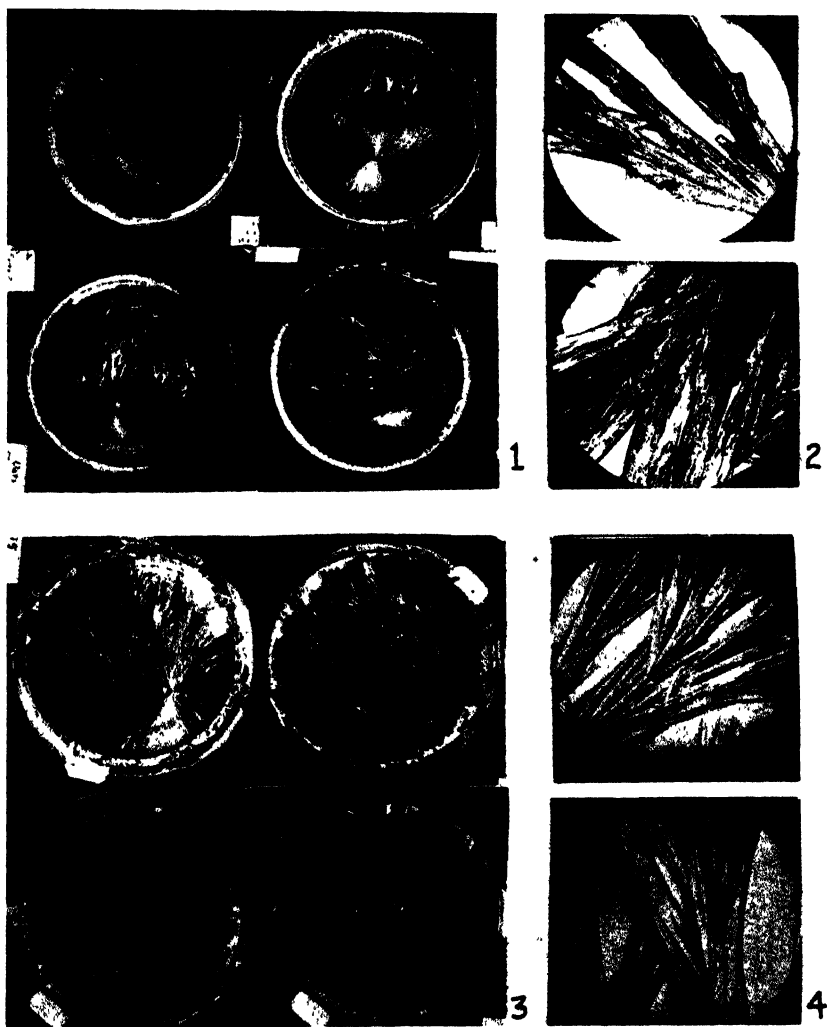
RESULTS

The solutions tested may be grouped into three classifications: (a) Those which have no influence, or practically none, on the crystallization of the cupric chloride. These include inorganic salts, simple sugars, glycine, and other substances of low molecular weight. (b) Those which produce a pattern characteristic of the substance used. Outstanding members of this class so far studied have been solutions of starch and glycogen, and extracts of the cereal grains. (c) Those which give a pattern with cupric chloride, but one which is non-specific. In this class have been most of the proteins studied, and some seed extracts; also cereal extracts that have autolyzed.

Most of the work so far has been done on the cereal grains. The extracts are made by grinding the grain either in a meat chopper or a mortar, then extracting with cold water, and filtering. The amount of water for extraction and the activity of the extract vary with the kind and grade of grain. Pfeiffer allows the grains to germinate for a few days before extraction. This does not affect the results appreciably.

Figure 1 shows the results with 0.2 cc. of an extract from oats, which was prepared with 5 parts of water and filtered or centrifuged. Figure 3 shows the results with 0.2 cc. of an extract from wheat, prepared with

3 parts of water. Figure 5 shows the results with 0.2 cc. of an extract from maize,¹ prepared with 2 parts of water. The differences between



FIGS. 1-4

FIG. 1. Effect of extract from oats

FIG. 2. Effect of extract from oats ($\times 28$)

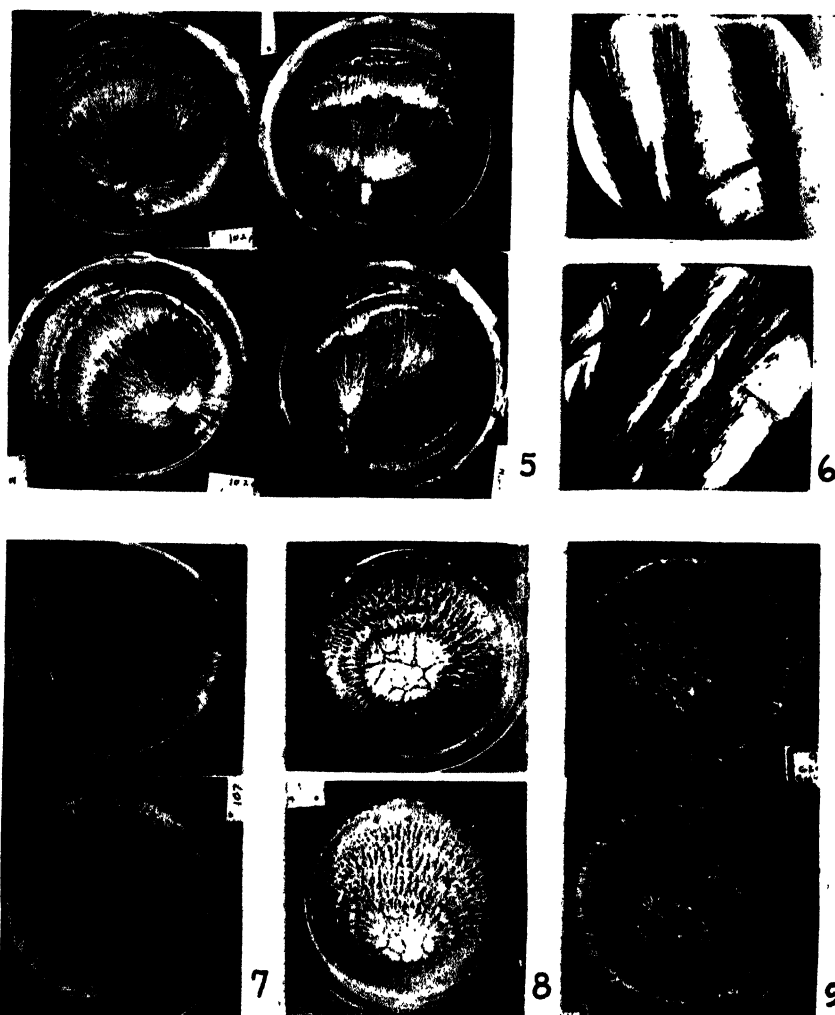
FIG. 3. Effect of extract from wheat

FIG. 4. Effect of extract from wheat ($\times 28$)

these are shown more strikingly by the photomicrographs in figures 2, 4, and 6.

¹ Golden Bantam sweet corn.

Figure 7 shows the results when a solution containing 40 mg. of glycogen was used. Figure 8 shows the results when a solution containing a solu-



FIGS. 5-9

FIG. 5. Effect of extract from maize

FIG. 6. Effect of extract from maize ($\times 28$)

FIG. 7. Effect of glycogen

FIG. 8. Effect of starch

FIG. 9. Effect of glucose

tion of wheat starch was used. There is no apparent difference in the patterns produced by starches from the different grains. Figure 9 shows the results with solutions containing 10 mg. and 1 mg. of glucose.

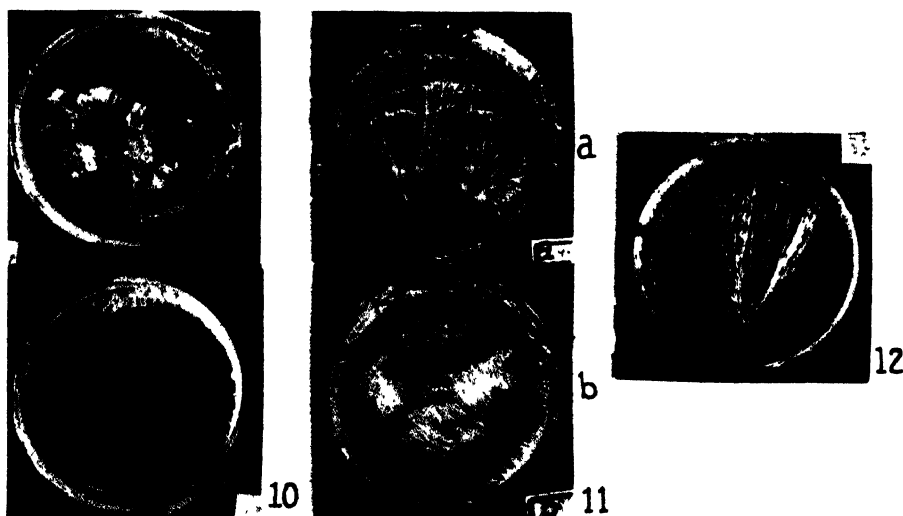
Figure 10 shows typical blanks.

Figure 11 shows the effect upon an extract from maize of the room in which the solutions evaporated. Figure 11a was obtained by evaporating the solution in an entirely enclosed room (a respiration chamber), and 11b was obtained at the same time with the same solution in an open room.

Figure 12 shows a typical non-specific pattern, obtained with hemolyzed blood.

CONCENTRATION OF AN ACTIVE FRACTION

The word "active" will be used subsequently to describe the ability of an extract to produce a characteristic crystal pattern with cupric chloride.



FIGS. 10-12

FIG. 10. "Blank"

FIG. 11. Effect of the room. (a) Evaporation in a respiration chamber;
(b) evaporation in an open room

FIG. 12 Non-specific

It has been found that the presence of enough protein in an extract produces only the non-specific pattern, and that if protein is added to an active preparation the non-specific pattern may overlay the characteristic one. An attempt has been made therefore to isolate an active fraction from oats, in the hope that methods could be developed that would be applicable to protein-containing solutions, with which so far the pattern has been non-specific.

Certain clues as to the nature of the active substance are given by the behavior of the extract. If it is kept at room temperature for 24 hr., the activity decreases, that is, the characteristic pattern gives place to the

non-specific one. This happens even in the presence of toluene, but does not occur if the fresh extract has been heated to 100°C. for 10 min. There is no loss of activity as a result of the heating. It is significant that the activity is entirely destroyed when the extract is incubated with "clarase" (a diastase) at 40°C. for 2 hr. Similar treatment with trypsin does not affect the activity. The activity is not lost on dialysis in a collodion sac.

A highly active preparation has been obtained by the following method: Oats are extracted with 5 parts of water, and the extract is evaporated at atmospheric pressure to about one-fifth of its volume. There is no loss of activity during this process. The precipitate of denatured protein is filtered off, and leaves a clear, straw-colored solution. This is saturated with ammonium sulfate, and the precipitate which appears is separated in the centrifuge or by filtration with suction, and is washed with saturated ammonium sulfate solution. The filtrate, when freed of ammonium sulfate by dialysis, is entirely inactive. The precipitate is taken up in a little hot water, and dialyzed to remove ammonium sulfate. A little material remains undissolved and may be removed in the centrifuge. The supernatant solution is poured into 5 volumes of 95 per cent alcohol, and the white precipitate produced is filtered off, washed first with 80 per cent, and then with 95 per cent alcohol, and is finally dried in a vacuum desiccator.

On one occasion 0.417 g. of this material was obtained from 125 g. of oats; 0.5 mg. of it gave the characteristic pattern with cupric chloride. Analysis (8) showed that the preparation contained 80 per cent of polysaccharide (calculated as $C_6H_{10}O_5$). The material contained sulfur, since when it was boiled with strong potassium hydroxide and subsequently acidified, a strong odor of hydrogen sulfide was produced. It gave a faint purple color when the biuret test was applied, and gave no coloration with iodine.

A rough assay of the activity of a preparation or extract is possible. For example, in one case 0.1-, 0.2-, 0.3-, and 0.4-cc. portions of an extract were used. The plate prepared with 0.1 cc. showed almost no recognizable pattern; those with 0.2- and 0.3-cc. portions showed a very faint but characteristic pattern; and the plate prepared with 0.5 cc. gave a clear strong pattern.

DISCUSSION

An hypothesis as to the cause of this phenomenon would be premature. Pfeiffer's speculations with respect to formative forces are not worthy of consideration on the basis of the experimental facts, however interesting they may be from a philosophical point of view. It is possible that variations in the surface tension may affect the crystallization, but the mapping out of surface tension lines into a coördinated pattern would still have to be explained.

Two other phenomena in nature are reminiscent of this one: the arrangement of iron filings in a magnetic field, and the figures of Chladni, caused by sound waves.

SUMMARY

Certain colloidal solutions have been found to exercise specific effects on the crystallization patterns produced by evaporation of aqueous solutions of cupric chloride under controlled conditions. In the case of oat extracts, the effect seems to be due to a polysaccharide.

An active fraction which gives the characteristic pattern has been isolated from oats.

We are indebted to Dr. H. B. Vickery, of the Connecticut Agricultural Experiment Station, for his criticism and advice; to Drs. H. E. Himwich and R. C. Dodge, of the Yale University School of Medicine, for the facilities they have provided; and to Dr. C. U. Linder and Mr. C. G. Morris for financial aid.

REFERENCES

- (1) ALEXANDER, JEROME: *Kolloid-Z.* **5**, 101 (1909).
- (2) ALEXANDER, JEROME: *J. Soc. Chem. Ind.* **28**, 280 (1909).
- (3) ALEXANDER, JEROME: *Kolloid-Z.* **4**, 86 (1909).
- (4) ALEXANDER, JEROME: *Science* **56**, 324 (1922).
- (5) ALEXANDER, JEROME: *Colloid Symposium Monograph* **1923**, 297.
- (6) ALEXANDER, JEROME: *Colloid Chemistry*, footnotes in Vols. 1 to 4.
- (7) ALEXANDER, JEROME: *Chemistry and Industry* **52**, 3 (1933).
- (8) Association of Official Agricultural Chemists, *Methods of Analysis*, XXVII, p. 31. Washington (1935).
- (9) DU NOÛY, P. LECOMTE: *Surface Equilibria of Biological and Organic Colloids*. The Chemical Catalog Co., Inc., New York (1926).
- (10) DU NOÛY, P. LECOMTE: in *Alexander's Colloid Chemistry*, Vol. II, p. 789. The Chemical Catalog Co., Inc., New York (1928).
- (11) MARRIAGE, ERNEST: *Kolloid-Z.* **11**, 1 (1912); *J. Roy. Soc. Arts* **61**, 371 (1913).
- (12) MICHAUD, F.: *J. chim. phys.* **33**, 828 (1936).
- (13) ORD, WILLIAM: *Crystallization and Cohesion*. London (1885).
- (14) PFEIFFER, EHRENFRIED: *Kristalle*. Orient-Occident Verlag, Stuttgart (1930).
- (15) PFEIFFER, EHRENFRIED: *Studien von Formkräften an Krystallization*. Dornach, Switzerland (1931).
- (16) PFEIFFER, EHRENFRIED: *Rev. gén. sci.* **47**, 424 (1936).
- (17) TRUMPP AND RASCHER: *Münch. med. Wochschr.* **83**, 1049 (1936).

CALCULATION OF APPROXIMATE PARTICLE SIZES IN STRATIFIED ALUMINA HYDROSOLS

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An outstanding characteristic of dispersed colloidal particles is that they tend to remain permanently dispersed. This tendency may be weakened, in practice, by continuous or discontinuous physical and chemical changes to the extent that the particles exhibit a more or less rapid sedimentation. Obviously, there will be a degree of stability extending from the infinitely stable sol to the extremely unstable one. This concept merely requires that, at some time during their existence, the sol particles possess a size that is in the colloidal range (11). Though it would at first appear that a physical stratification in sol systems would indicate a more or less measurable rate of precipitation, the broad concept noted above can be made to include stable systems which exhibit stratification in size or density.

Various workers have reported periodic sedimentation structures in gaseous and fluid media. Michalev (5), for example, found that boiled $\text{Al}(\text{OH})_3$ powder gives rise to periodic structures upon sedimentation in water. In fact, finely divided precipitates, especially of a gelatinous or semigelatinous character, will often exhibit stratification during gradual settling, without any special precautions being taken as to temperature or vibration. Alumina hydrosols, prepared from aluminum-copper couples, appear to be an example of a stable stratified sol system (6, 7).

The hydrosols were merely poured into settling tubes and allowed to stand undisturbed in a room where temperature changes were quite small. No effort was made to prevent the slight vibrations which normally exist in the average building, nor were the settling tubes shielded other than by placing them in a covered box. This indicates that stratification is often a specific property of the hydrosol, dependent primarily upon its past history and secondarily upon its environment (7).

RATE OF STRATIFICATION AND PARTICLE SIZE

Figure 1 portrays graphically the stratification data obtained on a typical alumina hydrosol prepared from an alcohol-activated, aluminum-copper couple (7). This sol contained 0.22 g. of aluminum oxide per liter.

Before the 2500-hr. period no stratification was apparent, and it is concluded that a kinetic adjustment of particle sizes was taking place. A fairly uniform zone settling velocity was exhibited during the 3000- to 3500-hr. period. After this the zone boundary gradually assumed a more or less permanent position, and an apparent equilibrium stratification resulted.

At the beginning of stratification each zone or cage may be considered to have a "reversed" screen for a bottom, that is, particles *larger* than a certain optimum size can pass through the boundary screen, but the smaller, optimum-sized particles are effectively held in the cage. After a uniform settling velocity for each boundary has been reached, each cage may be postulated to contain particles of only one size, that is, particles of an average, optimum size. The cages finally slow down and eventually

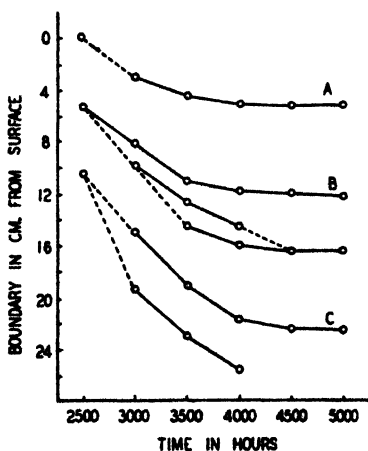


Fig. 1. Stratification in alumina hydrosols

reach "bottom", bottom being the equilibrium stratification level of each zone.

If this argument is accepted, Stokes' law (4, 10)

$$r^2 = \frac{9nh}{2gt(d_1 - d_2)} \quad (1)$$

may be applied to each cage, since each particle therein is of the same average size and will fall at approximately the same rate. In equation 1, r is the radius of a single (spherical) particle, n is the viscosity of the medium, h/t is the limiting velocity of fall, g is the gravity constant, and d_1 and d_2 are the densities of the particles and of the medium, respectively.

Table 1 summarizes some calculations based on equation 1, taking d_1 as 3, d_2 as 1.0, n as 0.01, g as 980, and considering the double cage C as a

single unit.¹ It will be noted that we have arbitrarily chosen to consider only three zones or cages during the present discussion. These are unique in that zone B starts at the height where zone A has reached its equilibrium value, and that zone C begins at the point where zone B leaves off. The few values given in table 1 serve merely as an example.

We note that the lower cages have a higher h/t value, which is to be expected if they are "heavier", i.e., filled with larger particles.² Furthermore, the particle size is about what would be expected for stable sols.³ Primary colloid particles are stated to have particle sizes ranging from 2 to 20 $m\mu$, and secondary colloid particles from 5 to 100 $m\mu$ (1). Burton has pointed out that silver particles (spherical) with a radius of 10 $m\mu$ settle at the rate of 2×10^{-7} cm. per second or 1 cm. in about 28 days (2), which is to be compared with a rate of 1.4 cm. in about 20 days for the alumina particles under consideration.

TABLE 1
Particle size from stratification data

CAGE	FROM THE STOKES EQUATION			FROM THE STOKES-EINSTEIN EQUATION	
	h per 500 hr.	r		Overall value of r	
		cm.	$m\mu^*$	cm.	$m\mu^*$
A.	1.4	4.2×10^{-6}	40	2.6×10^{-6}	30
B.	3.0	6.2	60		
C.	4.0	7.1	70		

*Approximate.

Einstein (3) has shown that if the time required by a particle to move from an initial to a final position be t , the mean value of the square of the displacement parallel to any direction of a spherical particle of radius r will be

$$D^2 = \frac{tRT}{3\pi nrN} \quad (2)$$

¹ The *Handbook of Chemistry and Physics* (The Chemical Rubber Co.) gives the densities of some aluminum oxides as follows: corundum (Al_2O_3), 4.0; aluminum oxide (Al_2O_3), 3.5-3.9; diaspor ($Al_2O_3 \cdot H_2O$), 3.4; gibbsite ($Al_2O_3 \cdot 3H_2O$), 2.4. The sol particles in the present case are almost certainly hydrated to some extent.

² Since no consideration is given to the number of particles in a given cage, "heavier" is in the sense of weight per particle, not the total weight of the cage. Actually, the weight of the individual particles determines the rate of fall.

³ It is of interest to note that colloidal copper prepared from an aluminum-copper couple was ultramicroscopically found to have an average particle size of 0.8 micron. Such particles settle quite rapidly (6).

where N is the Avogadro number, R and T have their usual significance, and the remaining symbols are as before. Should the random Brownian movement responsible for the displacement D in equation 2 be of such a magnitude as to neutralize the gravitational effect, the particles will obviously cease to settle. In such an event we can say that the Brownian displacement is equal to the gravitational fall. Thus, we equate the D of equation 2 against the h of equation 1 and obtain

$$r^3 = \frac{27nRT}{4\pi g^2 N(d_1 - d_2)^2} \quad (3)$$

with the symbols as already defined. Solving this equation for the radius, with the values as for equation 1, except that, in addition, $R = 8.3 \times 10^7$, $T = 300$, and $N = 6 \times 10^{23}$, we obtain the values given in the last two columns of table 1. These values, it will be seen, are in excellent agreement with the radii recorded in the preceding columns.⁴

Several other interesting and instructive calculations are likewise possible by the use of the stratification data obtained with alumina (and other) hydrosols of this type. With the limited data at hand, it will suffice to indicate briefly several such possibilities; one can readily extend specific calculations along the lines indicated.

Perrin (9) has applied the gas laws to colloidal suspensions to calculate N , the Avogadro number, employing the well-known equation

$$\log \frac{x_0}{x} = \frac{4\pi r^3 g l N (d_1 - d_2)}{6.9RT} \quad (4)$$

wherein x_0 and x denote the number of particles per unit volume at each of two planes, l units apart, with the remaining symbols designating units previously defined. Employing the radii calculated from the Stokes equation and the equilibrium zone-height, with other values as before, one is in a position to calculate the ratio x_0/x , i.e., the ratio of the number of particles at the top of a zone to the number of particles at the bottom of the same zone. Since the x_0/x ratio may be considered proportional to the number of particles in the zone under consideration, certain plausible assumptions based on expansions or progressions should lead to values for the total weight of material in the suspension.⁵

Sven Odén (8) has summarized some equations for distribution of size

⁴ If the Einstein equation is solved directly for r , with values of D ($=h$) and t as previously given, we obtain a radius one-tenth the value given above. It is apparent that the Einstein equation is not very accurate, since r varies as D^2 ; furthermore, a value of r calculated by the Einstein equation alone represents a limiting value, i.e., a value smaller than that obtained by any sedimentation data.

⁵ It should be noted that Perrin, in his calculations of N , used particles about 500 m μ in diameter, i.e., some ten times larger than those considered here.

and weight which may be applicable to the present case. We make the assumption that the rate of stratification is proportional to a given rate of sedimentation. Thus we calculate, for each individual zone, the percentage stratification ("sedimentation") at various time intervals, as given in table 2. It will be noted that the percentage order, i.e., percentage variation from A to B to C, is nearly perfect.

A plot of the percentage stratification values for each zone *versus* time results in three curves, each starting at zero percentage and 2500 hr., ending at 100 percentage and 5000 hr., with increasing curvature from zones A to C. Such a plot, by means of the well-known tangent method, allows the calculation of the percentage class size, i.e., the percentage of particles for corresponding radii ranges, based on the Stokes equation (10). The plot of percentage *versus* radii should give a Maxwellian distribution type of curve.

TABLE 2
Percentage stratification with time^a

ZONE	PERCENTAGE STRATIFICATION IN EACH ZONE (APPROXIMATE)					
	2500 hr.	3000 hr.	3500 hr.	4000 hr.	4500 hr.	5000 hr.
A	0	58	85	98	100	
B	0	41	81	94	97	100
C	0	37	72	93	99	100

SUMMARY

Calculations of particle sizes in an apparently stable, stratified, alumina hydrosol system, based on the rate of stratification, have given results which are of the correct order of magnitude. This suggests that whenever a rate of stratification is exhibited, Stokes' law, alone or in combination with Einstein's equation for Brownian movement, may be applied to the velocity of settling of zones. It has been briefly indicated how Perrin's and Odén's equations may be applied to stratifying systems in order to obtain information relative to the amount of material present and the percentage class size and size distribution of particles.

REFERENCES

- (1) ALEXANDER, J.: Colloid Chemistry, Vol. I, p. 14. The Chemical Catalog Co., Inc., New York (1926).
- (2) BURTON, E. F.: in Alexander's Colloid Chemistry, Vol. I, p. 165. The Chemical Catalog Co., Inc., New York (1926).
- (3) EINSTEIN, A.: Ann. Physik 17, 549 (1905); 19, 371 (1906); 22, 569 (1907); Z. Elektrochem. 14, 235 (1908).

^a It should be noted that in reference 7, from which these data are taken, table 2 should be corrected in columns 15 and 18, third line from the bottom, to read 6.3 and 6.2, in place of 16.3 and 16.2, respectively.

- (4) KELLEY, W. J.: *Ind. Eng. Chem.* **16**, 928 (1928).
- (5) MICHALEV, P. F.: *J. Phys. Chem. (U. S. S. R.)* **10**, 881 (1937).
- (6) MILLER, M. A.: *Kolloid-Z.* **77**, 310 (1937).
- (7) MILLER, M. A., *J. Phys. Chem.* **42**, 419 (1938).
- (8) ODÉN, S.: in *Alexander's Colloid Chemistry*, Vol. I, p. 861. The Chemical Catalog Co., Inc., New York (1926).
- (9) PERRIN, J.: *Compt. rend.* **146**, 967 (1908); **147**, 530, 594 (1908); **152**, 1390 (1911).
- (10) STOKES, C. G.: *Phil. Mag.* **29**, 60 (1846); *Trans. Cambridge Phil. Soc.* **3**, 287 (1849).
- (11) VON WEIMARN, P. P.: in *Alexander's Colloid Chemistry*, Vol. I, p. 27. The Chemical Catalog Co., Inc., New York (1926).

THE ADSORPTION OF COMPLEX AMMONIA IONS ON SILICA GEL

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The strong adsorption of complex metal amines by silica gel has been reported previously by Smith and Reyerson (5). By reduction of the adsorption products at elevated temperatures by hydrogen, metallic deposits are produced on the surface of the silica gel. These substances have proved to be very active catalytic agents in hydrogenation and other types of reactions, and the metal films of silver and nickel have been used by Smith and Reyerson (6) in streaming potential cells for measurement of electrokinetic potentials. Studies on the adsorption of the copper ammine on silica gel were made by Kolthoff and Stenger (2), who found that a final equilibrium condition is reached only after very prolonged shaking, and that the composition of the copper ammine ion undergoes a continuous change during the process. Reyerson and Clark (3) give results on the adsorption of the complex ammonio ions of silver and copper on silica gel, and report the influence of the pH of the equilibrium solution on the adsorption of the latter ion.

The present study was undertaken in order to determine the relative adsorption values of several of the common metal amines, namely, those of silver, nickel, copper, and zinc, since this knowledge would be of great value in preparing mixed metal surfaces on silica gel for future studies in catalysis. It was felt, also, that this adsorption phenomenon offered an excellent opportunity to obtain information regarding the nature of adsorption from complex mixtures and its relation to the adsorption of the individual components in simple solutions.

The adsorption isotherms for these four amines were first obtained. Next, the adsorption of each component in mixtures of all combinations of two, three, and four of these compounds was determined. In these mixtures the initial concentrations of all components in each mixture were equal, and the total concentration in every case was originally 1.0 *N*.

EXPERIMENTAL

The silica gel used in these experiments was obtained from the Silica Gel Corporation. It was treated with nitric and hydrochloric acids to

remove iron and other impurities, then washed with frequent changes of distilled water over a period of several days, and finally dried at 300°C. The resulting product was quite transparent and glassy in appearance.

The solutions of complex ammonio compounds were prepared from the nitrates of silver, nickel, copper, and zinc, which were of the best quality available commercially (C.P. grade or better) and were used without further purification. Approximately 1.0 *N* solutions of each were prepared in the following manner. The desired quantity of the salt was dissolved in distilled water. To this solution concentrated ammonium hydroxide was added carefully until the precipitate at first formed just dissolved, then an excess of 5 ml. per liter of final solution was added. The solution was then diluted with distilled water to the correct volume. It was noted that practically identical amounts of ammonium hydroxide were added for equal volumes of solutions of the four metal salts. The resulting solutions were assumed to contain $\text{Ag}(\text{NH}_3)_2^+$, $\text{Cu}(\text{NH}_3)_4^{++}$, $\text{Ni}(\text{NH}_3)_4^{++}$, and $\text{Zn}(\text{NH}_3)_4^{++}$, and were, respectively, colorless, dark blue, medium blue, and colorless. It is quite possible that the nickel solution may have contained a small amount of the hexammine compound, but the color of the latter (pale violet) was not evident. Bjerrum (1) has shown that these solutions are quite complex, so it is probably impossible to obtain a pure solution containing but a single compound.

Solutions of lower concentration were prepared by diluting the above stock solutions.

Each sample for study was prepared as follows: 15.00 g. of silica gel was weighed into a 125-ml. Erlenmeyer flask (coated internally with paraffin wax to prevent reaction between ammonia and the glass), and 75.00 ml. of solution was added. The flask was stoppered with a paraffined cork stopper and placed in a shaking machine (4).

The experiments were carried on in a room in which the temperature varied little from 25°C.

The methods of analysis of the original solutions and of the final equilibrium solutions were the following standard procedures: (1) *Silver*: precipitation as silver chloride and weighing in filtering crucibles of Jena glass. (2) *Nickel*: precipitation as nickel dimethylglyoxime and weighing as above. (3) *Copper*: iodometric titration in acetic acid solution with sodium thiosulfate which had been standardized with pure copper. (4) *Zinc*: titration in sulfuric acid solution with potassium ferrocyanide, standardized with pure zinc, using diphenylamine as internal indicator. (5) *Separations*: in the case of mixtures, silver was always removed first by precipitation as silver chloride; copper was removed (when present) by precipitation in hydrochloric acid solution with hydrogen sulfide; nickel and zinc, when simultaneously present, were then separated by precipitating nickel dimethylglyoxime in the presence of some excess ammonium

chloride, and subsequently precipitating the zinc in the filtrate with hydrogen sulfide, followed by filtration, solution, and titration.

The amounts of metal adsorbed per gram of silica gel were determined by calculation from the decrease in concentration as determined in the analyses. Analyses of the silica gels after adsorption were not made as some experimenters have done, for it was believed that it would be impossible to wash the gel surface (both external and internal) free of the solution without disturbing the adsorbed material and introducing unpredictable complications as a result.

RESULTS AND DISCUSSION

It was found that these systems, especially in the cases of the more concentrated solutions, were slow to reach an equilibrium condition. This is in agreement with the results of Kolthoff and Stenger on the adsorption of the copper ammine. The time required to reach equilibrium approx-

TABLE 1

Influence of the time factor on the amount of silver complex ammine adsorbed on silica gel

INITIAL CONCENTRATION (NORMALITY)	FINAL CONCENTRATION (EQUILIBRIUM)	MILLIEQUIVALENTS ADSORBED PER GRAM OF SILICA GEL	TIME OF ADSORPTION
<i>milliequivalents per milliliter</i>	<i>milliequivalents per milliliter</i>	<i>milliequivalents</i>	<i>hours</i>
0.9822	0.7777	1.021	4
0.9988	0.7948	1.019	5
0.9988	0.7932	1.027	9
1.0001	0.7931	1.035	77

ently depends upon the concentration, and also largely upon the complexity of the system in question, since it is comparatively small for the silver ammine, which is obviously the simplest case. Table 1 shows the amounts adsorbed after various periods of time from solutions which were originally about 1.0 *N*. Note that the amount adsorbed after 77 hr. is practically identical with that after 4 hr., especially considering the difference in original concentrations. These results also indicate that the method of preparing the solutions of amines gives quite uniform products, since three separately prepared solutions were used here.

The results of adsorption studies on four complex amines (silver, nickel, copper, and zinc) are presented in table 2. In each case the values for the more concentrated solutions were obtained after 77 hr. of shaking with the silica gel.

These results are presented graphically in figures 1 and 2, in which the isotherms are drawn. The nearly linear relationship shown by the graphs

of the logarithms of the amounts adsorbed (figure 2) is in close agreement with the empirical isotherm of Freundlich. The change in slope of these curves at the higher concentrations seems to be characteristic of all these systems. It might be thought to indicate that the adsorption had not yet reached a constant value, but this seems improbable in the light of the results of table 1. A wide variation in the specific adsorption values of

TABLE 2
Adsorption of complex amines on silica gel
Temperature, 25°C. (approx.)

INITIAL CONCENTRATION (NORMALITY)	FINAL CONCENTRATION (EQUILIBRIUM)	MILLIEQUIVALENTS ADSORBED PER GRAM OF SILICA GEL
I. Silver ammino ion, $\text{Ag}(\text{NH}_3)_2^+$		
<i>milliequivalents per milliliter</i>	<i>milliequivalents per milliliter</i>	<i>milliequivalents</i>
1.0001	0.7931	1.035
0.4911	0.3269	0.820
0.3274	0.1898	0.687
0.2455	0.1274	0.590
II. Nickel ammino ion, $\text{Ni}(\text{NH}_3)_4^{++}$		
1.0070	0.6545	1.763
0.4888	0.1851	1.517
0.3259	0.0697	1.279
0.2444	0.0251	1.095
III. Cupric ammino ion, $\text{Cu}(\text{NH}_3)_4^{++}$		
0.9886	0.3488	3.199
0.4428	0.0185	2.121
0.2972	0.0035	1.469
0.2234	0.0012	1.111
IV. Zinc ammino ion, $\text{Zn}(\text{NH}_3)_4^{++}$		
1.0229	0.1717	4.256
0.5096	0.0142	2.475
0.3410	0.0038	1.686
0.2548	0.0012	1.267

these four solutes is readily noted. The adsorption of the zinc ammine is particularly outstanding, and this fact is borne out in the ensuing studies on the mixtures of these compounds.

It is worthy of mention, also, that if we were to plot the millimoles adsorbed instead of milliequivalents, the values for nickel and silver would be very nearly the same. In general, it seems that we may classify the zinc and copper amines together as being very highly adsorbed, the

silver and nickel ammines being more moderate in degree of adsorbability. Results on mixtures will be seen to lead to the same rough classification.

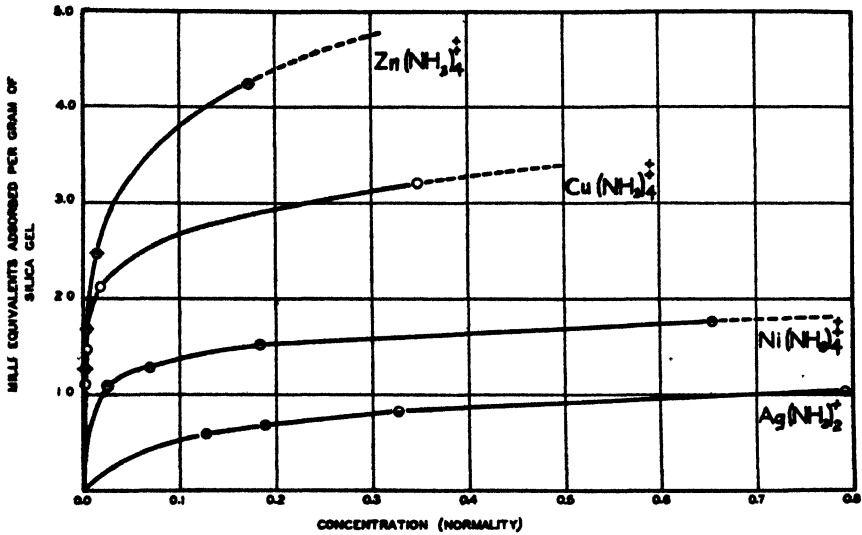


FIG. 1. Adsorption isotherms for metal ammines on silica gel

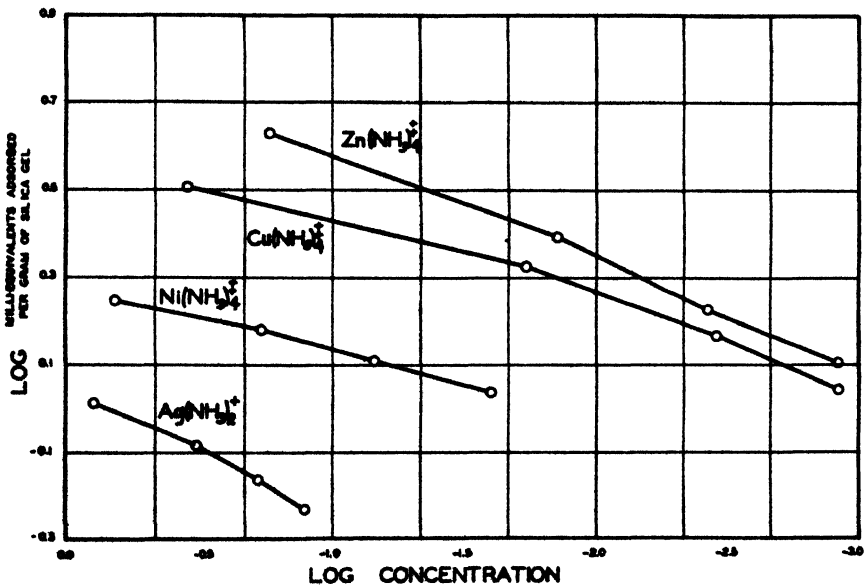


FIG. 2. Adsorption isotherms for metal ammines on silica gel

Solutions consisting of two of the above ammines, each of 0.5 *N* concentration, i.e., with a total concentration of 1.0 *N*, were prepared and the

adsorptions on silica gel measured. The appropriate solutions of mixed solutes were in all cases prepared first and then added to the silica gel. The results are given in table 3. In figure 3 these values are shown graphically in such a manner that the influence on each metal ammine of the presence of the other amines, arranged in order of increasing adsorbability, is demonstrated. In particular it will be noted that the relative order of adsorption is the same as in the case of the simple solutions, and that the adsorption of the zinc ammine is practically uninfluenced by the presence of other solutes. The zinc ammine is almost

TABLE 3
*Adsorption from mixtures of two complex amines**
Total concentration, 1.0 N; temperature, 25°C. (approx.)

EXPERIMENT	AMMINES IN SOLUTION	INITIAL CONCENTRATION	FINAL CONCENTRATION	MILLIEQUIVALENTS ADSORBED PER GRAM OF SILICA GEL
		<i>milliequivalents per milliliter</i>	<i>milliequivalents per milliliter</i>	<i>milliequivalents</i>
I	$\text{Ag}(\text{NH}_3)_2^+$	0.5000	0.4017	0.491
	$\text{Ni}(\text{NH}_3)_4^{++}$	0.5000	0.3133	0.933
II	$\text{Ag}(\text{NH}_3)_2^+$	0.4972	0.4162	0.405
	$\text{Cu}(\text{NH}_3)_4^{++}$	0.4972	0.0678	2.147
III	$\text{Ag}(\text{NH}_3)_2^+$	0.5000	0.4273	0.363
	$\text{Zn}(\text{NH}_3)_4^{++}$	0.5000	0.0281	2.359
IV	$\text{Ni}(\text{NH}_3)_4^{++}$	0.4989	0.3450	0.769
	$\text{Cu}(\text{NH}_3)_4^{++}$	0.4989	0.1810	1.589
V	$\text{Ni}(\text{NH}_3)_4^{++}$	0.5000	0.4280	0.360
	$\text{Zn}(\text{NH}_3)_4^{++}$	0.5000	0.0415	2.333
VI	$\text{Cu}(\text{NH}_3)_4^{++}$	0.5000	0.2650	1.175
	$\text{Zn}(\text{NH}_3)_4^{++}$	0.5000	0.0313	2.343

* Time of adsorption in each case, 9 hr.

completely adsorbed in all three cases in which it occurs. On the other hand, the amount of silver, nickel, and copper adsorbed is distinctly decreased by the presence of other amines. The repressing influence in each case increases with increasing adsorbability of the other ions, i.e., in the order silver, nickel, copper, and zinc.

Table 4 gives the results of experiments dealing with mixtures of three and four of the amines, in which the total concentration was 1.0 N and the initial concentration of all ions in any given solution was the same. In figures 4 and 5 these results are presented graphically as in the

above case. Again the almost complete adsorption of zinc ammine is observed, and also the slight influence of the other solutes on this particular one. In each case a more or less marked decrease in amount of any particular ion adsorbed in the presence of other ions of increasing adsorbabilities is noted. It can also be shown by simple arithmetic that the amount of a given ion adsorbed in a complex mixture of ions can be predicted with an accuracy of about 5 to 10 per cent by averaging the values found in simpler mixtures of the same ions. Further study of this relationship is to be undertaken in the future in other experiments of this nature. It is also apparent that the values obtained in the mixture of all

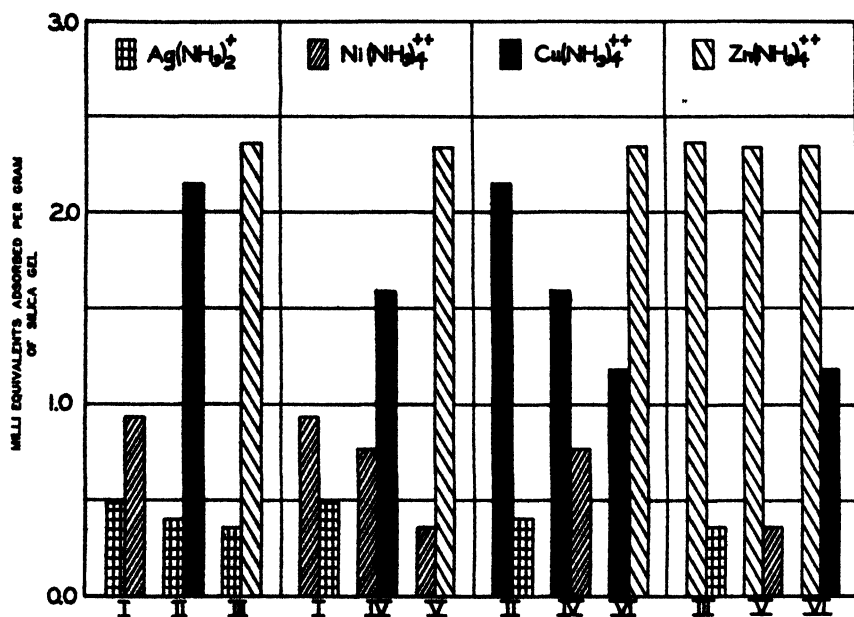


FIG. 3. Adsorption from mixtures of two solutes. Total concentration, 1.0 normal

four ammonies are of the same relative magnitude as those indicated in the simple solutions of table 2 and figure 1.

That the ammonies are adsorbed in polymolecular layers of approximately colloidal thickness is known as a result of x-ray studies on the metallized gels obtained by reduction of the adsorbed ammonies by hydrogen. Such studies have yielded the typical metal crystal patterns in the cases of silver and nickel, the only ones studied by this means by the author (6).

The adsorption in the case of all of the mixtures was determined for the same time period,—namely, 9 hr. While it is likely that a final equilibrium value was not attained in this time, still it seems that this is not

of much importance in the present study. The time of adsorption was, of course, the same for each ion in the mixture and was sufficient to show the relative adsorption values clearly. In line with the results of Kolthoff and Stenger, it seems that the slowness in reaching a final constant state is due to the occurrence of chemical changes in the adsorbed layer following the initial adsorption of the complex ion, rather than to a low adsorption rate. The near-equilibrium value which is attained in a few hours is thus

TABLE 4
*Adsorption from mixtures of three and four complex amines**
Total concentration, 1.0 N; temperature, 25°C. (approx.)

EXPERIMENT	AMMINES IN SOLUTION	INITIAL CONCENTRATION	FINAL CONCENTRATION	MILLIEQUIVALENTS ADSORBED PER GRAM OF SILICA GEL
		milliequivalents per milliliter	milliequivalents per milliliter	milliequivalents
VII	$\text{Ag}(\text{NH}_3)_2^+$	0.3329	0.2716	0.307
	$\text{Ni}(\text{NH}_3)_4^{++}$	0.3329	0.2054	0.637
	$\text{Cu}(\text{NH}_3)_4^{++}$	0.3329	0.1007	1.161
VIII	$\text{Ag}(\text{NH}_3)_2^+$	0.3333	0.2747	0.293
	$\text{Ni}(\text{NH}_3)_4^{++}$	0.3333	0.2538	0.397
	$\text{Zn}(\text{NH}_3)_4^{++}$	0.3333	0.0010	1.661
IX	$\text{Ag}(\text{NH}_3)_2^+$	0.3333	0.2826	0.253
	$\text{Cu}(\text{NH}_3)_4^{++}$	0.3333	0.1250	1.041
	$\text{Zn}(\text{NH}_3)_4^{++}$	0.3333	0.0052	1.641
X	$\text{Ni}(\text{NH}_3)_4^{++}$	0.3333	0.2584	0.375
	$\text{Cu}(\text{NH}_3)_4^{++}$	0.3333	0.1620	0.857
	$\text{Zn}(\text{NH}_3)_4^{++}$	0.3333	0.0102	1.615
XI	$\text{Ag}(\text{NH}_3)_2^+$	0.2500	0.2037	0.231
	$\text{Ni}(\text{NH}_3)_4^{++}$	0.2500	0.1786	0.357
	$\text{Cu}(\text{NH}_3)_4^{++}$	0.2500	0.1053	0.723
	$\text{Zn}(\text{NH}_3)_4^{++}$	0.2500	0.0064	1.218

* Time of adsorption in each case, 9 hr.

likely to offer a truer representation of the primary adsorption of complex ions than the final equilibrium value, which is reached only after many weeks or months. Preparations are in progress for a detailed study of the effect of the time factor and also the pH factor on these adsorption phenomena, particularly in the mixtures. In the latter case it is apparent that, although the pH values of the various solutions used in the present study probably differed somewhat, nevertheless all ions in any given mixture were adsorbed at the same pH value.

It was found that no appreciable amount of silica was dissolved under the conditions of these experiments. This differs from the results of Kolthoff and Stenger but is logical, since the relative quantities of solution and silica gel used were so vastly different from those used by these authors.

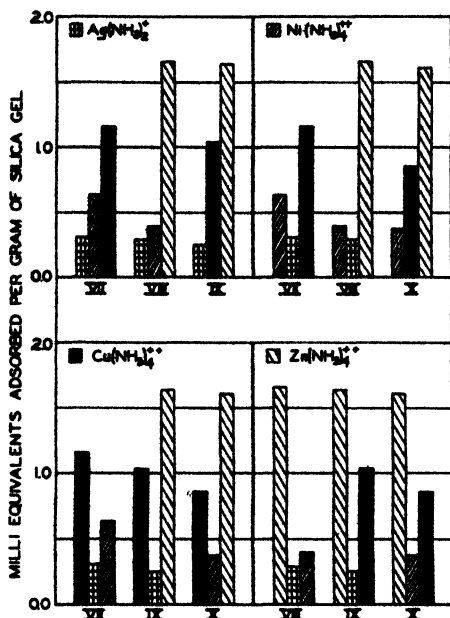


FIG. 4

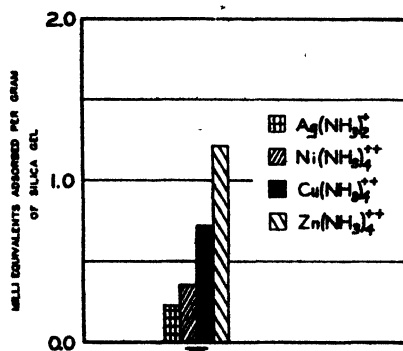


FIG. 5

FIG. 4. Adsorption from mixtures of three solutes. Total concentration, 1.0 normal
FIG. 5. Adsorption from mixture of four solutes. Total concentration, 1.0 normal

SUMMARY

1. The adsorption isotherms of the complex ammonio ions of silver, nickel, copper, and zinc on silica gel have been determined.
2. The adsorption of the same ions from mixtures of two, three, and four components, originally at a total concentration of 1.0 N, has also been measured.
3. In all cases the adsorption in milliequivalents per gram of silica gel was greatest for the zinc ammine, and decreased in the following order: zinc, copper, nickel, and silver.
4. The time required to reach a constant state in the adsorption of silver ammine is considerably shorter than that for the divalent complex ions, and was about 4 hr. or less.
5. In the mixtures the adsorption of each component is dependent upon the specific adsorption characteristics of the other components present,

i.e., it is decreased in the presence of highly adsorbable ions, and the amount of decrease is greater the greater the adsorbability of the other components.

6. The zinc ammine, which exhibits very strong adsorption, is only slightly less adsorbed in the presence of the other amines studied.

7. Knowledge of the adsorption characteristics of the individual solutes, alone and in simple mixtures, enables one to predict, at least qualitatively, the behavior in more complex mixtures of the same solutes.

CONCLUSION

It is hoped that much insight into the nature of the adsorption behavior of these and other complex ammonio ions, as well as information concerning the nature and composition of the amines themselves, may be gained in further studies now contemplated. The author also plans to carry out experiments to determine the catalytic behavior of the metal catalysts obtained upon reduction by hydrogen of the adsorption products resulting from the present work. The determination of the character of these metallic deposits in the case of the mixed amines is also to be undertaken by x-ray methods, and should be of considerable value in explaining the phenomena.

REFERENCES

- (1) BJERRUM, J.: Kgl. Danske Videnskab. Selskab, Math.-fys. Medd. 11, No. 5 (1931); 11, No. 10 (1932); 12, No. 15 (1934).
- (2) KOLTHOFF, I. M., AND STENGER, V.: J. Phys. Chem. 38, 475 (1934).
- (3) REYERSON, L. H., AND CLARK, R. E.: J. Phys. Chem. 40, 1055 (1936).
- (4) SMITH, G. W.: Ind. Eng. Chem. 10, 282 (1938).
- (5) SMITH, G. W., AND REYERSON, L. H.: J. Am. Chem. Soc. 52, 2584 (1930).
- (6) SMITH, G. W., AND REYERSON, L. H.: J. Phys. Chem. 38, 133 (1934).

A STUDY OF THE REACTIONS OF SILK FIBROIN WITH ACID AND BASIC DYES¹

EDNA CHRISTINE HOFFMAN WITH PAULINE BEERY MACK

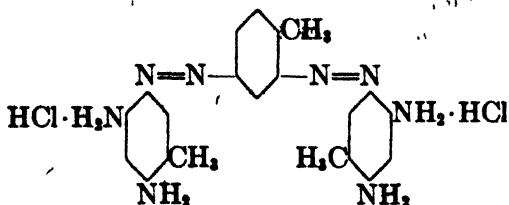
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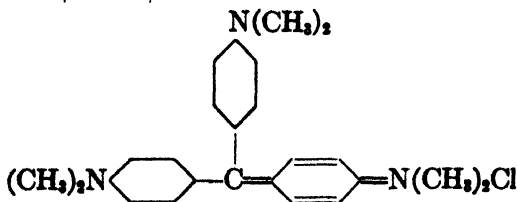
INTRODUCTION

The investigation described in this report involves a theoretical study of the dyeing properties of a group of acid and of basic dyes when applied to silk fibroin. Some of the acid dyes were matched in molecular structure as nearly as possible with basic dyes, so that the chief differences between certain of the dyes used were in their acidic or basic groups.

Two azo dyes and five triphenylmethane dyes were selected. The formulas for the dyes are given below, together with the Colour Index Number of each (18).

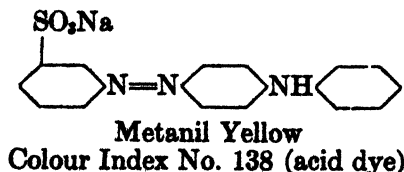
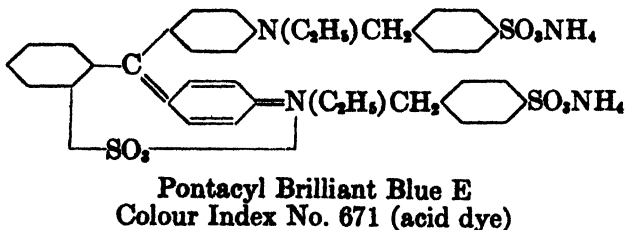
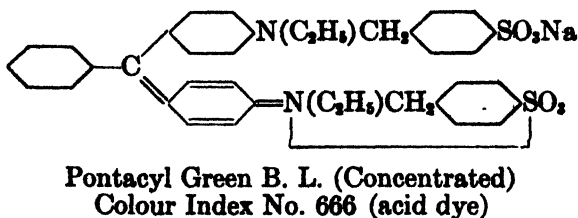
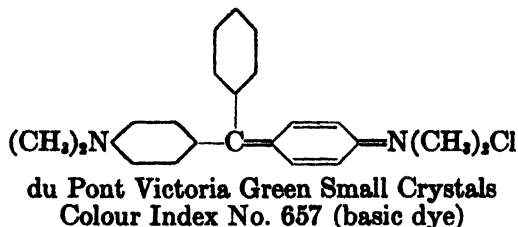
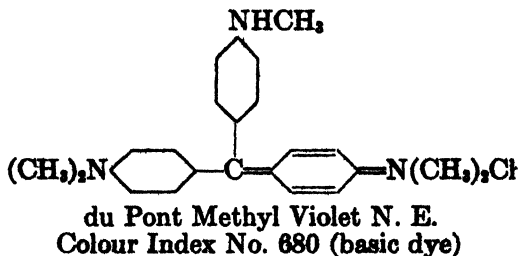


du Pont Basic Brown BX
Colour Index No. 332 (basic dye)



du Pont Crystal Violet Extra Pure APN
Colour Index No. 681 (basic dye)

¹ This is Paper No. 4 in a series of reports on the reactions of textile fibers with dyes of various chemical types, based on work carried on in the Textile Chemistry Laboratories, Department of Chemistry, The Pennsylvania State College. This study was carried on by the junior author in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry, August, 1937.



The work was divided into the following parts: (1) A study of the effect of temperature, of time, of concentration, and of initial pH on the amount of dye taken up by a unit weight of fibroin. (2) A study of the changes of hydrogen-ion concentration that took place during the dyeing processes as carried out in the concentration and pH studies.

PROCEDURE AND EXPERIMENTAL RESULTS

The fibroin used was a pure dye silk crêpe fabric from which the sericin had been removed by a boiling-off process. The fibroin samples were treated with successive baths of hot distilled water until there was no further change in the pH of the rinse solution. The samples were then brought to constant weight within a precision of ± 0.005 g.

The dyes were purified by recrystallization from water and from alcohol.

Throughout the study a dye bath of 250 cc. was used. Distilled water was employed in making up the dye solutions, and no substance other than dye was added to the bath except in the part of the work in which the initial pH of the bath was changed. This was brought about by adding the quantities of hydrochloric acid or of sodium hydroxide required to obtain the desired pH.

The concentrations of the dye baths were determined by titration with titanium trichloride, a method studied by Knecht and Hibbert (10),

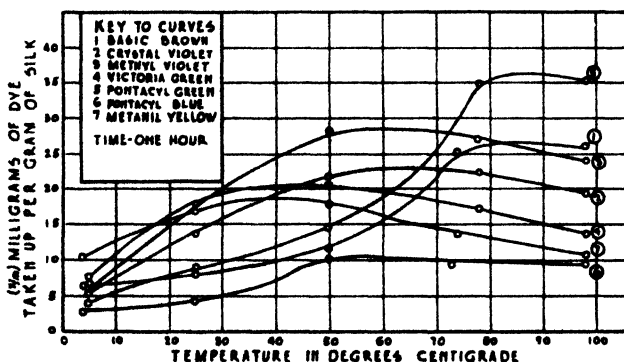


FIG. 1. The effect of temperature on dye take-up

modified by Calcott and English (2), and further modified as to mechanical details in this laboratory.

Temperature studies

Dyeing procedures were carried out at five temperatures, which were kept under thermostatic control at 2–4°C., 25°C., 50°C., 75°C., and 97°C. A summary of the data secured in dyeing silk fibroin at these various temperatures with the seven dyes listed in the introduction is shown graphically in figure 1.

A temperature of 25°C. was selected as satisfactory for the remainder of the study. Thermostatic control of this temperature was maintained.

Time studies

In the time studies, samples were dyed for periods of 2, 4, 8, or 16 hr. The results obtained from the studies on time in relation to dye take-up

are shown in figure 2. From this figure it can be seen that equilibrium has been reached at or near the end of an 8-hr. period at a temperature of 25°C. This time, therefore, was selected for the remainder of the study.

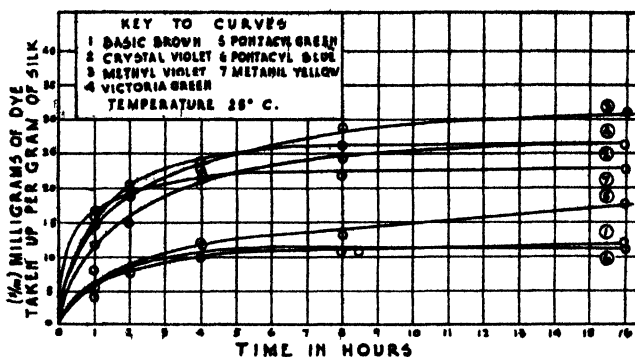


FIG. 2. The effect of time on dye take-up

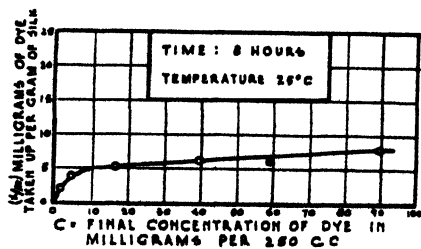


FIG. 3

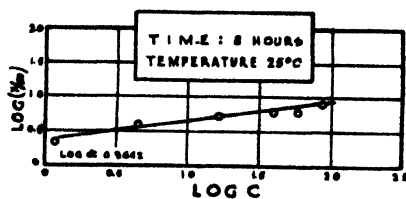


FIG. 3A

FIG. 3. The effect of concentration on the take-up of Basic Brown by silk
FIG. 3A. Logarithmic curve for Basic Brown

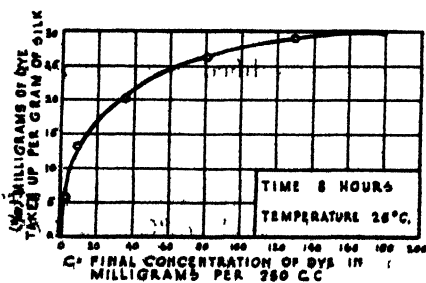


FIG. 4

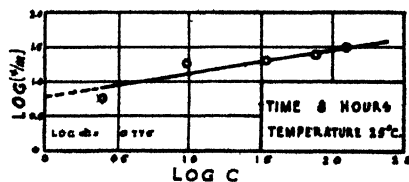


FIG. 4A

FIG. 4. The effect of concentration on the take-up of Crystal Violet by silk
FIG. 4A. Logarithmic curve for Crystal Violet

Concentration studies

A series of dyeings was then made for each of the dyes at 25°C., for an 8-hr. period, in which the initial concentration of the dye bath was varied. In figures 3 to 9, inclusive, the effect of the initial concentration

of the dye bath on the quantity of dye taken up per unit weight of fabric is shown graphically. Since it was desirable to find whether or not the

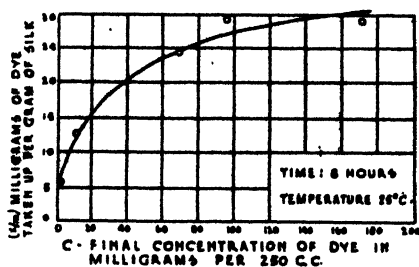


FIG. 5

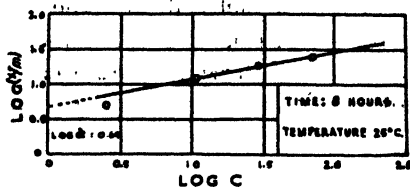


FIG. 5A

FIG. 5. The effect of concentration on the take-up of Methyl Violet by silk
FIG. 5A. Logarithmic curve for Methyl Violet

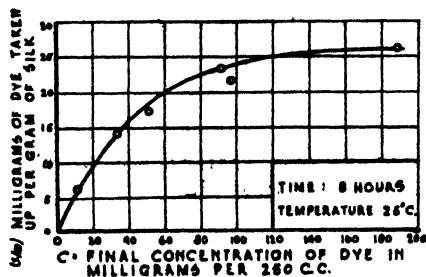


FIG. 6

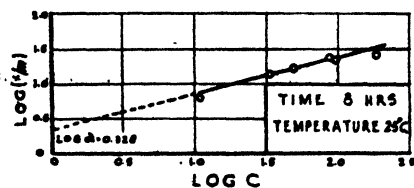


FIG. 6A

FIG. 6. The effect of concentration on the take-up of Victoria Green by silk
FIG. 6A. Logarithmic curve for Victoria Green

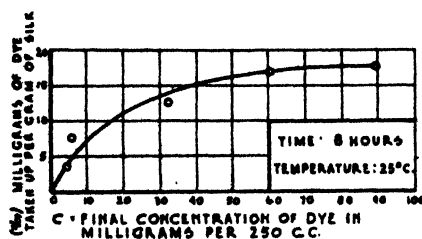


FIG. 7

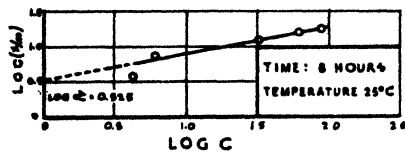


FIG. 7A

FIG. 7. The effect of concentration on the take-up of Pontacyl Green by silk
FIG. 7A. Logarithmic curve for Pontacyl Green

relationship between the amount of dye taken out of the bath per unit weight of silk and the equilibrium concentration of dye conformed to the Freundlich equation for adsorption (4), which is

$$\frac{x}{m} = \alpha C^{1/n}$$

logarithmic curves of take-up against equilibrium concentration were plotted. These are shown in figures 3A to 9A.

In the studies on dye concentration the initial and the final pH of each bath was measured by means of a Leeds and Northrup portable potentiometer electrometer, Number 7666, fitted with a glass electrode and a saturated calomel cell, and the change in hydrogen-ion concentration in the bath resulting from the removal of dye by the fibroin was calculated. The results of these pH measurements and of the calculations of change in hydrogen-ion concentration are shown in table 1.

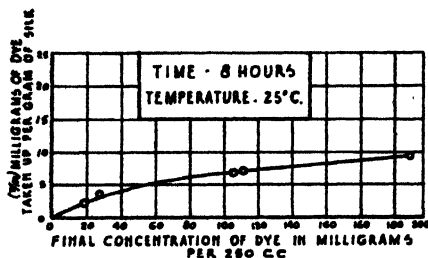


FIG. 8

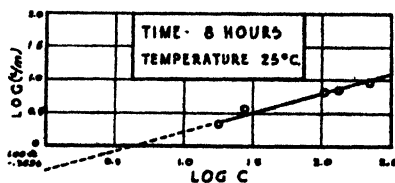


FIG. 8A

FIG. 8. The effect of concentration on the take-up of Pontacyl Blue by silk
FIG. 8A. Logarithmic curve for Pontacyl Blue

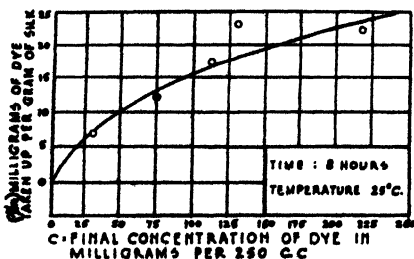


FIG. 9

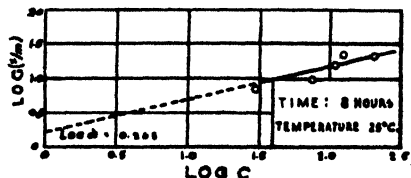


FIG. 9A

FIG. 9. The effect of concentration on the take-up of Metanil Yellow by silk
FIG. 9A. Logarithmic curve for Metanil Yellow

pH studies

The effect of the initial pH of the bath on the amount of dye taken up per gram of silk, plotted for each dye individually, is shown in figure 10. In this figure the initial pH and the final pH are plotted separately against the amount of dye taken up per unit weight of fibroin, and the direction of the pH shift for each determination is shown by means of arrows.

The effect of initial pH upon the change in hydrogen-ion concentration of the bath is plotted separately for each dye in figure 11. In each case two curves are shown, one representing the change in hydrogen-ion concentration with different initial pH values obtained when the silk was im-

TABLE 1

Change in hydrogen-ion concentration during dyeing of silk fibroin with various basic dyes in baths of different concentrations

Time, 8 hr.; temperature, 25°C.

DYE	SAMPLE NUMBER	INITIAL DYE CONCENTRATION	g/m (MG. OF DYE TAKEN UP PER GRAM OF FIBROIN)	INITIAL pH	FINAL pH
Basic Brown.....	1	10.03	2.14	3.86	3.98
	2	23.44	4.07	3.87	3.67
	3	40.12	5.31	3.66	3.41
	4	69.11	6.22	3.54	3.39
	5	85.57	6.05	3.42	3.39
	6	123.13	8.01	3.45	3.39
Crystal Violet.....	1	28.67	5.89	5.61	4.21
	2	61.80	13.39	5.46	3.60
	3	123.07	20.27	4.94	3.54
	4	192.38	26.53	4.96	3.47
	5	273.75	29.27	4.68	3.31
Methyl Violet	1	28.33	5.80	4.94	3.86
	2	63.00	12.75	4.78	3.47
	3	110.90	18.73	4.47	3.34
	4	179.85	24.41	4.33	3.24
	5	231.70	29.12	4.24	3.12
Victoria Green ..	1	41.40	6.36	3.58	3.51
	2	91.80	14.14	3.30	3.30
		134.54	17.23	x	x
	3	190.86	23.47	3.05	3.00
	4	200.90	17.23	3.18	3.13
	5	354.25	21.56	3.02	2.98
Pontacyl Green.....	1	21.47	3.65	5.66	5.30
	2	38.84	7.64	5.74	5.36
	3	89.20	12.58	5.74	5.35
	4	132.60	16.96	5.64	5.27
	5	165.83	17.61	5.65	5.25
Pontacyl Blue.....	1	26.02	2.21	5.57	5.13
	2	45.88	3.98	5.27	5.14
	3	134.38	6.64	5.66	5.54
	4	161.80	7.30	5.07	5.11
	5	260.30	9.50	4.99	5.07
Metanil Yellow.....	1	61.55	7.33	x	x
	2	126.17	12.45	5.58	5.92
	3	187.55	17.54	5.47	6.03
	4	219.93	22.99	5.54	6.07
	5	341.75	21.81	5.47	6.03

mersed in distilled water solutions containing varying quantities of hydrochloric acid or sodium hydroxide but no dye, and the other representing similar changes for the bath containing the dye.

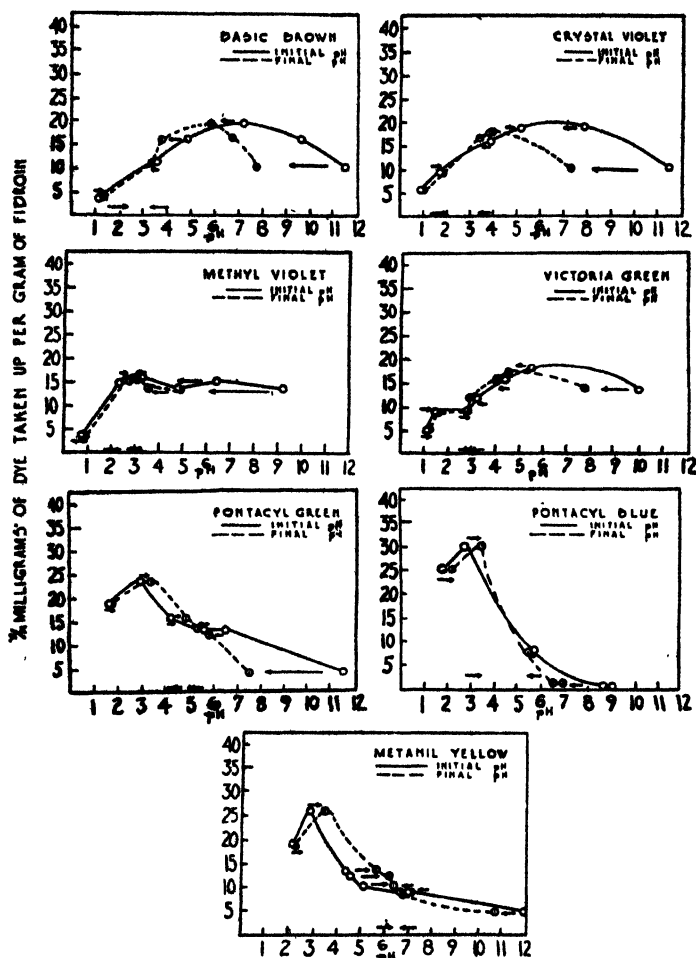


FIG. 10. Effect of initial pH on the take-up of dye by the fibroin, together with the shift of pH during the dyeing of fibroin in baths of different pH values.

DISCUSSION

The effect of concentration on dye take-up

Freundlich and Losev (5) have shown that the removal of dye by carbon and by textile fibers is primarily an adsorption phenomenon and that it follows the empirical equation

$$\frac{x}{m} = aC^{1/n}$$

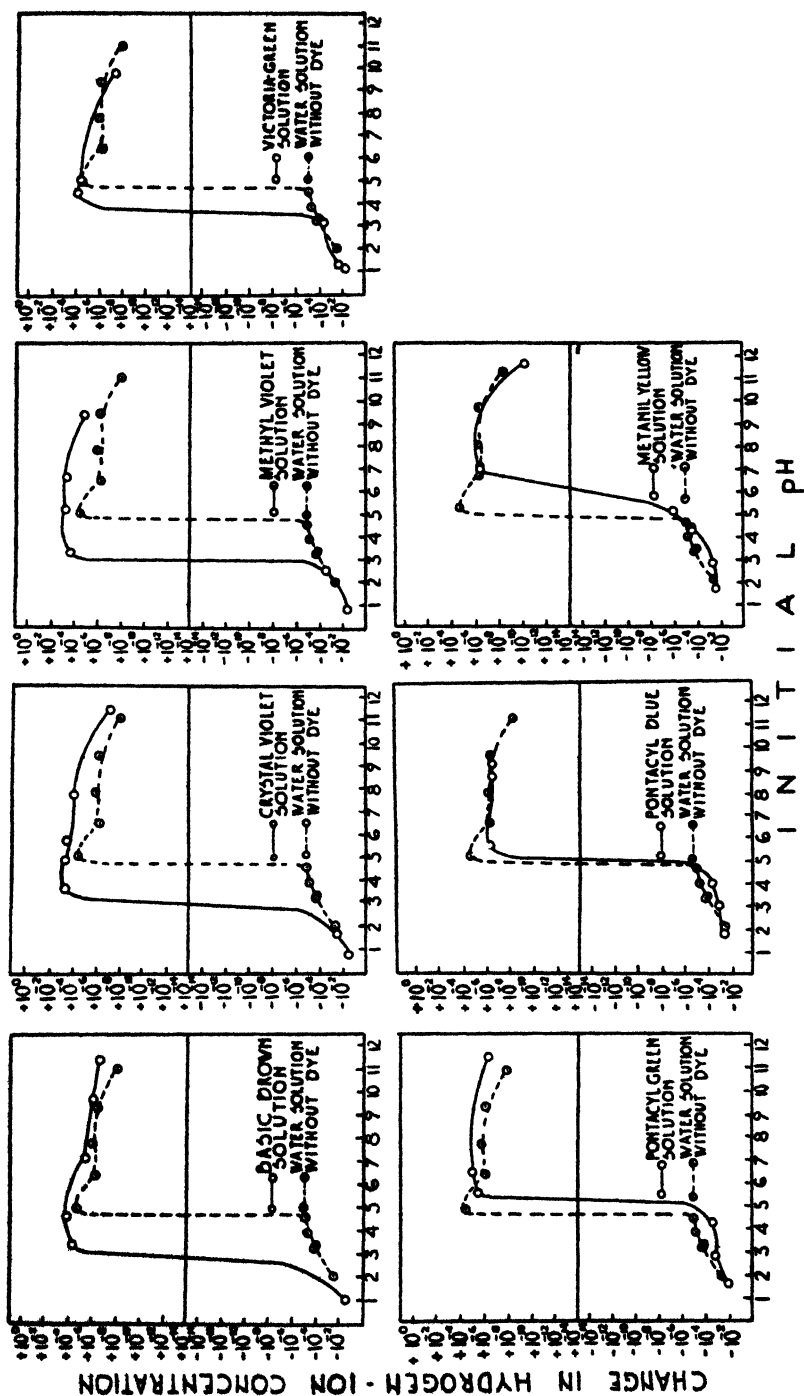


Fig. 11. Effect of initial pH upon the change in the hydrogen-ion concentrations of dye baths of different initial pH values

where x/m is equal to the weight in grams of adsorbed material taken up per gram of adsorbent, α is a constant representing the dye taken up per unit weight of adsorbent at unit concentration, C is the concentration of dye at equilibrium, and $1/n$ is a constant peculiar to the adsorbent and the adsorbed substance, and numerically equal to the slope of the line obtained by plotting $\log x/m$ against $\log C$. The dyeing of silk with acid and basic dyes was found by Houck (7) to take place in accordance with this adsorption theory. Likewise, the take-up of acid and basic dyes by wool was reported by Briggs and Bull (1) as an adsorption process, and the dyeing of wool with Metanil Yellow and with Methylene Blue was found by Parks and Beard (12) to be the same type of reaction.

Pfeiffer and coworkers (14, 15, 16) have been able to form compounds between simple azo, keto, and quinone dyes and phenylalanine, sarcosine, and sarcosine anhydride, and have concluded from this work that dyeing is due to the formation of chemical compounds at the surface of the fiber.

Porai-Koshitz (17) boiled silk and wool in solutions of ammonium chloride containing acid and substantive dyes in the form of sodium salts. He found that the amount of ammonia set free was equivalent to the amount of dye acid fixed by the fiber; this result lends support to the theory that the dyeing of animal fibers consists of the formation of salts of the fibers and the dye acid.

Harris and Smith (6) have determined the dye-combining capacity of untreated wool for an acid dye, Orange II, and have shown it to be equal to the acid-combining capacity of the wool. Treatments with nitrous acid, hydrogen peroxide, sodium hypochlorite, and strong sulfuric acid decrease the basicity of the wool and likewise its dyeing capacity. These authors present their data as further evidence in favor of the chemical theory of wool dyeing.

In the present investigation, the relationship between the amount of each of the dyes taken up by the silk fibroin and the equilibrium concentration of the dye bath was studied. Reference to figures 3A to 9A shows that the logarithmic graph is a straight line in every case. It can be concluded, therefore, that, under the conditions studied, the dyeing of silk with Basic Brown, Crystal Violet, Methyl Violet, Victoria Green, Pontacyl Green, Pontacyl Blue, and Metanil Yellow is an adsorption process, although this conclusion does not necessarily preclude the possibility of chemical union between surface micelles of the fiber and the adsorbed dye.

Examination of figures 3 to 9 shows that the amount of dye adsorbed at a definite concentration apparently does not depend on the acidity or basicity of the dye molecule. It appears, also, that no direct relationship

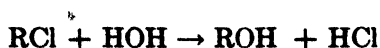
exists between the type of dye (whether azo or triphenylmethane) and the amount of dye adsorbed at a given concentration. The complexity of the dye molecule, however, may have an effect upon the amount of dye taken up, in that a dye with a more elaborate structure may be adsorbed to a lesser degree than one which is less complex.

Among the basic dyes, for example, the three triphenylmethane dyes—Crystal Violet, Methyl Violet, and Victoria Green—are adsorbed in larger quantity per unit weight of fibroin than is Basic Brown. The latter has two diazo groups in addition to three phenyl groups.

The presence of the diazo groups is not solely responsible for the lesser degree of take-up, because Metanil Yellow, the one acid dye with a diazo group, is adsorbed to the greatest degree of any of the acid dyes. The remainder of the Metanil Yellow molecule, however, is simple in structure in comparison with the two triphenylmethane dyes,—Pontacyl Green and Pontacyl Blue. The higher adsorption of Pontacyl Green in comparison with Pontacyl Blue may be accounted for at least in part by the presence of two sulfonate groups in the former and three in the latter.

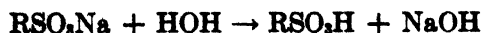
Changes in pH during dyeing

In the study of the effect of dye concentration on the proportion of dye taken up, the results with the various dyes, as presented in table 1, show that the solutions of the four basic dyes decreased in pH as the concentration was increased. This is to be expected, if we consider the dye as a salt of a weak base and of a strong acid. If this were the case, hydrolysis would cause the following reaction to occur:



This reaction would result in the formation of the strongly ionized hydrochloric acid and a weak base, ROH. More hydrochloric acid would be formed by hydrolysis as the concentration of dye bath was increased; and increase in concentration of dye, therefore, should cause the pH to decrease. This has been found to be the case. Parks and Beard (12) have found similar results with another basic dye,—Methylene Blue.

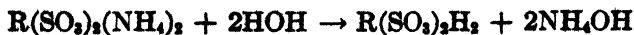
If we consider the acid dyes—Metanil Yellow and Pontacyl Green—to be salts of a sulfonic acid and of sodium hydroxide, the type hydrolysis equation would be the following:



Neither of these dyes showed notable changes in initial pH with concentration changes within the range of concentrations studied. This indicates either that these dyes do not hydrolyze to an appreciable extent, or that,

if they hydrolyze, the acid and base formed may be of sufficiently similar degree of ionization to neutralize or balance each other, resulting in no change in pH.

Pontacyl Blue is the ammonium salt of a complex sulfonic acid, and may hydrolyze as follows:



Since ammonium hydroxide is a poorly ionized base, it is possible that the ionization of the dye acid exceeds that of the base. If this be the case, it explains the fact that the pH decreased with increasing dye concentrations.

The shift in pH during dyeing in baths containing the dye alone with no auxiliary reagent was not great in any of the dyes, and was virtually independent of the amount of dye removed from the bath by the fibroin. Parks and Beard (12) obtained the same results with Metanil Yellow and with Methyl Violet on wool. Elöd (3) found that the action of Crystal Violet on wool results in an increased pH of the dye bath after dyeing, which is independent of the amount of dye taken out of the bath.

The effect of initial pH on dye adsorption

Figure 10 shows that the initial pH of the dye bath had a pronounced effect upon the amount of dye adsorbed per unit weight of fibroin for each of the dyes studied. The effect is similar for all of the basic and for all of the acid dyes, but differs markedly for the two types of dyes.

The amounts of the basic dyes, Basic Brown, Crystal Violet, and Victoria Green, taken up by the silk increase with an increase in hydroxide ion to a value of pH 6 to 8, above which the quantity of dye adsorbed is decreased with further increases in hydroxide ion. The quantity of Methyl Violet taken up increases to pH 4 to 8, above which it decreases. The increase of the basic dye adsorption with increase in hydroxide ion is understandable if the hydrolysis equation proposed for this group of dyes in an earlier part of this report is correct, since an increase in hydroxide ions in the bath would tend to cause more of the dye base to be formed. It would appear that this increase should continue, rather than fall off after a maximum was reached. Another variable condition was encountered in this connection, however, in that each of the basic dyes showed visible evidence of flocculating within the pH range at which the increase in dye adsorption ceased, as well as at higher pH values.

The amounts of each of the acid dyes, Pontacyl Green, Pontacyl Blue and Metanil Yellow, that were taken up per unit weight of fibroin increased as the hydrogen-ion concentration of the bath was increased, from the highest pH studied down to pH 2.5 to 3.5. If the hydrolysis equations previously given for the acid dyes are correct, it is to be expected that an

increase in the acidity of the bath would cause an increase in the dye acid which is formed. This would probably have continued through the pH range studied were it not for the fact that the particle size of the dye in solution changed as the pH of the bath was decreased beyond the pH range of 2.5 to 3.5. Metanil Yellow showed flocculation at pH 2.84 and below. Although Pontacyl Blue and Pontacyl Green did not show visible flocculation within the pH range studied, Pontacyl Blue changed color at pH 2.2 and below, and Pontacyl Green at pH 3.0 and below,—evidence of change of particle size.

Pelet-Jolivet and Siegrist (13) found that dye take-up increased with an increase of electrolyte up to a maximum, beyond which further addition of electrolyte caused a decrease in the amount of dye taken up. Parks and Bartlett (11) found that the addition of hydrochloric acid to a Metanil Yellow bath increased the adsorption of this dye by a textile fiber, which they explained as due to the common hydrogen ion. Unpublished work in this laboratory in which wool was dyed with Metanil Yellow showed results similar to those under discussion.

Johnson and Harris (8) and Johnson and Hawley (9) found the isoelectric point of silk fibroin to be between pH 2.1 and pH 2.2. The data upon which figure 10 is based do not show any apparent relationship between the isoelectric point of silk and the amount of dye removed from the different baths through a wide range of initial pH values.

Change in hydrogen-ion concentration during dyeing in baths of different initial pH

In figure 10 the initial and the final pH values of the dye baths may be compared throughout the pH range studied. In all cases the fibroin took a larger amount of hydrogen than of hydroxide ion out of the bath at low pH values, and a larger amount of hydroxide than of hydrogen ion at higher pH values. The pH value at which the transition occurred between the raising and the lowering of the pH value of the bath as a result of the dyeing operation was between pH 2 and 3 for all of the basic dyes, between pH 4 and 5 for Pontacyl Green and Pontacyl Blue, and between pH 6 and 7 for Metanil Yellow.

Figure 11 shows the effect of the initial pH upon the change in hydrogen-ion concentration during dyeing for each of the dyes studied; this change is plotted on a logarithmic scale. The unbroken line in each of the graphs represents the change of hydrogen-ion concentration which occurred with the dye bath in question. The broken line represents the change which took place as a result of immersing silk fibroin in a distilled water bath containing the quantity of hydrochloric acid or sodium hydroxide needed to give the desired initial pH value, but no dye.

In preparing the series of baths used as the water solution in this part

of the study, hydrochloric acid was added in different amounts to solutions below pH 5, and sodium hydroxide was added above this point. These two reagents were added as needed to produce the desired initial pH in the dye solutions.

When dye is absent, the broken curve shows that the hydrogen-ion concentration of the bath becomes less as a result of the immersion of fibroin therein, at pH 5 and below, and greater above this pH value. This may have resulted from the adsorption of hydrochloric acid and of sodium hydroxide from their respective solutions. The fact that a change in pH is brought about by immersing silk in water solutions of acids and bases of different initial pH values is in agreement with the results of Elöd (3), who obtained pH changes by immersing wool in water solutions to which reagents had been added to give different pH values, but in which no dye was present.

The dyes have an effect upon the change in hydrogen-ion concentration of the dye baths in addition to that of the acid and alkali in the bath, as may be seen from the fact that the two graphs do not coincide throughout the pH range studied. With all of the basic dyes, the point at which the fibroin ceases to reduce and begins to increase the concentration of hydrogen ion is at a lower pH than was found with baths alike in all other respects except that the dye was absent. If it is accepted that basic dyes hydrolyze in solution with the formation of the dye base and hydrochloric acid, then the removal of the dye base from solution should lower the pH value at which the concentration of hydrogen ions ceases to decrease and begins to increase.

Furthermore, the increase in hydrogen-ion concentration should be greater for each initial pH value with the dye present than without it. This was found to be the case.

With the acid dyes hydrolysis has been shown as probably resulting in the formation of a sulfonic acid, together with sodium hydroxide in the case of Pontacyl Green and of Metanil Yellow, and ammonium hydroxide in the case of Pontacyl Blue. When these dyes are added to the other components in the baths, the pH range at which the fibroin ceases to remove products the removal of which causes a decrease in hydrogen-ion concentration and begins to remove those the removal of which causes an increase in concentration of hydrogen ion is in the direction opposite to that found with the basic dyes, but is not so pronounced. Moreover, the decreases in hydrogen-ion concentration are slightly greater than those in the baths not containing the dye, and the increases are very slightly greater in almost all cases, although the amount of change in hydrogen-ion concentration is practically the same whether the acid dyes are present in the bath or not. An exception is found in the case of Pontacyl Green

at pH 6 or more, above which range the increase in hydrogen-ion concentration is somewhat augmented by the presence of the dye.

It should be noted in this connection that the acid dyes used in the study differ from the basic dyes in that the acid and basic products of ionization are probably not so widely different in degree of ionization as are the products of ionization of the basic dyes. Moreover, the acid dyes are not entirely comparable with respect to each other as to the products which they form upon hydrolysis.

SUMMARY

The foregoing report is a description of the dyeing properties of four basic and three acid dyes on silk fibroin.

Changes in the temperature of the dye bath and of the time of immersion were found to have a marked effect upon the amount of dye taken up by the fibroin for each of the dyes, but the effect was not uniform. Equilibrium was reached for all of the dyes in a period of 8 hr. at 25°C., and these conditions were used throughout the remainder of the study.

The dyeing reaction with each of the seven dyes studied was found to conform to Freundlich's adsorption isotherm under the conditions employed, insofar as the amount of dye taken out of baths of different initial concentration per unit weight of silk fibroin was concerned.

Changes of pH with change in concentration of dye are explained on the basis of hydrolysis of the dye. Changes of pH during dyeing, which have been found to be independent of the amount of dye taken up by the silk, are discussed.

Changes brought about in the hydrogen-ion concentration of baths differing widely in initial pH values by immersing silk fibroin therein are reported and discussed in detail.

REFERENCES

- (1) BRIGGS, T. R., AND BULL, A. W.: *J. Phys. Chem.* **26**, 845-75 (1922).
- (2) CALCOTT, W. S., AND ENGLISH, F. L.: *Ind. Eng. Chem.* **15**, 1042-4 (1923).
- (3) ELÖD, E.: *Chem. Zentr.* **97**, II, 2632-3 (1926).
- (4) FREUNDLICH, H.: *Colloid and Capillary Chemistry* (English translation), 3rd edition. E. P. Dutton and Company, New York (1926).
- (5) FREUNDLICH, H., AND LOSEV, G.: *Z. physik. Chem.* **59**, 284-312 (1907).
- (6) HARRIS, M., AND SMITH, A.: *Am. Dyestuff Repr.* **26**, 416 (1937).
- (7) HOUCE, R. C.: *J. Phys. Chem.* **32**, 161-86 (1928).
- (8) JOHNSON, T. B., AND HARRIS, M.: *Ind. Eng. Chem.* **22**, 539-42 (1930).
- (9) JOHNSON, T. B., AND HAWLEY, T. G., JR.: *Ind. Eng. Chem.* **22**, 297-99 (1930).
- (10) KNECHT, E., AND HIBBERT, E.: *New Reduction Methods in Volumetric Analysis*. Longmans, Green and Company, London, England (1925).
- (11) PARKS, L. R., AND BARLETT, P. G.: *Am. Dyestuff Repr.* **24**, 476 (1935).
- (12) PARKS, L. R., AND BEARD, H. C.: *Am. Dyestuff Repr.* **24**, 558-61 (1935).

- (13) PELET-JOLIVET, L., AND SIGRIST, H.: *Z. Chem. Ind. Kolloide* **5**, 235-7 (1909) through *Chem. Abstracts* **4**, 829 (1910).
- (14) PFEIFFER, P., AND ANGERN, O.: *Z. angew. Chem.* **39**, 253-9 (1926).
- (15) PFEIFFER, P., AND COWORKERS: *J. prakt. Chem.* **126**, 97-145 (1930) (through *Chem. Abstracts* **24**, 3498 (1930)).
- (16) PFEIFFER, P., AND WANG, L.: *Z. angew. Chem.* **40**, 983-91 (1927).
- (17) PORAI-KOSHITZ, A. E.: *J. Soc. Dyers Colourists* **52**, 19 (1936).
- (18) ROWE, F. M.: *Colour Index*, 1st edition. The Society of Dyers and Colourists, Bradford, Yorkshire, England (1924).

THE SURFACE ENERGY OF MIXTURES OF FINELY DIVIDED CARBON AND PARAFFIN

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The way in which a finely divided solid behaves in some respects like a liquid, e.g., in that it can be poured and assumes the shape of the vessel, is well known and suggests that the cohesive forces between solid particles would set up a "surface tension" resembling that of a liquid with very large molecules. The measurement of such an effect is, however, impracticable, but the cohesive forces are operative and produce a measurable effect when the particles are mixed with a heavy liquid such as paraffin. It is found that a remarkably large increase in surface energy occurs when finely divided carbon is mixed with paraffin; indeed, liquids are produced of surface energy greater than that of any other liquids excepting the liquid metals. This increase is a beautiful example of the transmission of forces from solids through liquid media, which has been studied by the writer in the case of adsorbed films on solids, and also for films on mica (3, 4). The theory for the cohesive forces between solid particles developed by the writer and others (2, 8) may be applied. The effect is a very large one, and it would seem that it provides a method of characterizing finely divided solid catalysts.

EXPERIMENTAL

The source of carbon was lampblack. The solid was free from ash and contained only a little hydrocarbon and water, which were removed by baking out in a high vacuum. Dry air was then admitted to the cooled solid, and portions were weighed out and thoroughly mixed with weighed quantities of paraffin. The mixture was evacuated by means of a Hyvac pump in order to remove the superficial air on the particles, and the surface "tension" was determined.

The method adopted was a slightly modified form of that due to Lenard (9). The pull required to remove a fiber from the surface was determined by means of an analytical balance. The quartz fiber of radius 0.007 cm. was joined to the quartz frame as in figure 1, and was under tension. The vertical portions projecting beyond the fiber preserve the edge of the film when the latter is drawn upwards. By means of the hooks X and Y

weights can be added to the frame so that the latter may be truly horizontal, as judged by the nature of the contact made when the pane is lowered slowly into the liquid. The small portions A and B are under the liquid, but the effect of the hydrostatic upthrust on these may be shown to be negligible.

Under these conditions

$$\sigma = \frac{W' - W}{2(l - 2r)} - r \left(\frac{l + 3r}{l} \right) \left[\frac{(W' - W)W}{l} \right]^{1/2} + r^2 \rho \left(1 + \frac{\pi}{4} \right) \quad (1)$$

where σ is the surface tension, l the length of the fiber, and r its radius, W' the weight of the frame at breaking point, and W the weight of the frame in air. In actual practice the second and third terms are negligible, and

$$\sigma = \frac{W' - W}{2(l - 2r)} \quad (2)$$

Hence a knowledge of the density of the liquid is not required.

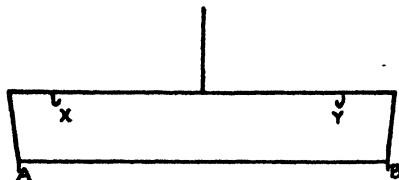


FIG. 1. Quartz frame and fiber

It was found that when mixtures of high concentration of solid were used it was necessary to deflect the balance beam carefully by hand until the breaking point was nearly reached. Then the weights were adjusted so that a slight increase in weight caused the rupture of the film after waiting some time.

The size of the particles was estimated by means of the eye-piece graticule due to Cawood and Patterson (5). A sample of the powder was shaken with benzene, and a drop of the liquid produced was quickly wiped across a microscope coverslip. In this way an even sooty film which was just visible by the naked eye was produced. The density of the particles was determined, using benzene as a covering liquid, and was found to be 1.66. A typical result is shown for 21°C. σ is the surface tension of the mixture and σ_L that of pure paraffin (see table 1).

The mean radius of the particles was 4.5×10^{-6} cm. This small size is essential for the success of the experiment. Thus finely divided metals, such as aluminium and magnesium, and finely divided substances, such as magnesium carbonate and zinc oxide, had no influence on the surface tension of paraffin, even though quite viscous mixtures were produced,

because the particles were insufficiently small. This result is in some respects fortunate, in that it confirms the correctness of the experimental procedure with carbon, for it would seem that with care the increased viscosity of the mixture does not prejudice the value of the surface tension, a constant value of which is obtained with these coarser powders over the entire range from fluid to viscous mixtures.

Finely divided solids of sufficiently small radius may, however, be prepared by the ignition of various salts, as it is well known that, provided the temperature is not too high, the shattered lattice does not aggregate to

TABLE 1

CARBON	$\sigma - \sigma_L$	$\frac{x}{(CF. EQUATION 12)}$	$1/[x^2(x-1)]$	CALCULATED VALUES OF $1/[x^2(x-1)]$
weight per cent	dynes per centimeter			
0	0		0	
18.5	0.5	1.897	0.588	0.86
24.1	5.0	1.720	0.806	0.895
25.2	6.2	1.690	0.854	0.90
27.3	12.8	1.640	0.953	0.95
29.9	31.7	1.584	1.083	1.075
31.0	42.2	1.562	1.139	1.145
32.0	52.0	1.543	1.194	1.210

TABLE 2

CUPRIC OXIDE	$\sigma - \sigma_L$	NICKEL OXIDE	$\sigma - \sigma_L$
weight per cent	dynes per centimeter	weight per cent	dynes per centimeter
0	0	40.5	1.4
25.4	1.5	48.7	14.7
36.4	5.8	50.1	26.6
37.8	11.0	51.5	37.1
38.7	28.0	53.1	82.0
40.7	33.2		
41.3	49.5		

give large particles. The carbonates of nickel and copper were heated in an electric furnace at 300°C., and were simultaneously evacuated. Considerable exaltation of the surface tension of paraffin was observed (see table 2). With magnesium carbonate the oxide produced gave no increase in surface tension. The temperature was 21°C. The radius of the particles was *circa* 5×10^{-5} cm.

The results are similar to those of von Antropoff (11), who measured the pull between two glass tubes coated with the mixture. von Antropoff used the method to obtain pastes of high surface tension, and did not explore the phenomenon itself.

THEORETICAL DISCUSSION

It was shown by the writer that the attractive force between two spheres of radii r_1 and r_2 is given by

$$\frac{4\pi^2 q^2 \lambda}{(n-1)(n-3)(n-4)(n-5)} \frac{1}{d^{n-5}} \left(\frac{r_1 r_2}{r_1 + r_2} \right) \quad (3)$$

where q is the number of molecules per cubic centimeter and d is the smallest distance between the surfaces of the spheres. The law of attractive force is $\lambda/(\text{intermolecular distance})^n$. Hamaker (8) and Derjaguin (6) have also studied the problem.

Expression 3 may be used to calculate the energy required to separate the mixture of solid particles and liquid into two halves, and thereby form two new surfaces. The work required to separate to infinity two equal spheres of radius r , with centers $d + 2r$ from one another is

$$\frac{2\pi^2 q^2 \lambda}{(n-1)(n-3)(n-4)(n-5)(n-6)} \frac{r}{d^{n-6}} = B_{ss} \frac{r}{d^{n-6}} \quad (4)$$

where the constant

$$B_{ss} = \frac{2\pi^2 q^2 \lambda}{(n-1)(n-3)(n-4)(n-5)(n-6)} \quad (5)$$

As the packing of the spheres in the liquid will be very roughly hexagonal, the above result (equation 4) should be replaced by

$$\frac{3\sqrt{3}}{4} \frac{r B_{ss}}{d^{n-6}} \quad (6)$$

It may similarly be shown that the work for separating a sphere from a plane is

$$2B_{ss} \frac{r}{d^{n-6}} \quad (7)$$

These expressions involving only neighboring spheres may be applied at once to the liquid mixture, since the law of force between particles separated by liquid films decays rapidly. A similar simplification has recently been applied by Wassajerna (12) in calculating the lattice energy of crystals.

The work of separating the two halves may be divided into the work of separating (a) the solid portions from one another, (b) the solid particles from liquid on the opposite sides of the dividing plane, and (c) the liquid from liquid. (b) may be further subdivided by imagining that the solid particles on one side of the plane are removed and the holes filled with liquid, and that the whole of the liquid is removed on the *other side*, leaving the solid particles. Then the work (b) will be twice the work of separating

this new system — twice the work of separating liquid from solid spheres. Similarly, the work for (c) may be divided by imagining all the spheres to be removed and replaced by liquid. Then the work of separation (actually the free energy for the isothermal separation) (cf. 7) is $2\sigma_L$.

Hence the work for (c) is $2\sigma_L$ — the work of separating the liquid spheres. It follows that

$$2\sigma = 2\sigma_L + \frac{3}{4}\sqrt{3}n_1 \frac{r}{d^{n-6}} (B_{ss} - B_{LL} - 2B_{sL}) + 4n_1 B_{sL} \frac{r}{(d/2)^{n-6}} \quad (8)$$

where n_1 is the number of solid particles per square centimeter of interface, and

$$B_{sL} = \frac{2\pi^2 q_s q_L \lambda_{sL}}{(n-1)(n-3)(n-4)(n-5)(n-6)} \quad (9)$$

For convenience the value of n is taken to be the same as for pure liquid and solid, as is suggested by quantum mechanics. The process of separation is of course idealized, and the liquid is split halfway between the solid spheres. Similarly the particles are imagined to be evenly distributed and of equal size.

Now d clearly depends on the percentage composition of the mixture (m = weight per cent of solid). Let ρ_s and ρ_n and ρ be the densities of solid, pure liquid, and mixture. Let n_s = the number of solid particles per cubic centimeter. Then the weight of the particles in 1 cc. is equal to

$$\frac{4}{3}\pi r^3 \rho_s n_s = \frac{m\rho}{100} \quad (10)$$

Moreover

$$\frac{4}{3}\pi \left(r + \frac{d}{2}\right)^3 n_s = 0.74 \quad (11)$$

for hexagonal close packing. Hence

$$\frac{(r + d/2)^3}{\rho_s r^3} = \frac{74}{m\rho} \quad \text{and} \quad r + d/2 = r \left[\frac{74\rho_s}{m\rho} \right]^{1/3}$$

Hence

$$d = 2r(x - 1)$$

where

$$x = \left(\frac{74\rho_s}{m\rho} \right)^{1/3} \quad (12)$$

Hence

$$\begin{aligned}\sigma - \sigma_L &= \frac{3}{8} \frac{\sqrt{3} n_1 r}{d^{n-6}} (B_{ss} - B_{LL} - 2B_{SL}) + \frac{2n_1 B_{SL} r}{(d/2)^{n-6}} \\ &= \frac{3}{8} \sqrt{3} (B_{ss} - B_{LL} - 2B_{SL}) \frac{2r}{\sqrt{3} 4x^2 r^2 [2r(x-1)]^{n-6}} \\ &\quad + \frac{4B_{SL} r}{\sqrt{3} 4x^2 r^2 [r(x-1)]^{n-6}} \\ &= \frac{3}{16} \frac{(B_{ss} - B_{LL} - 2B_{SL})}{x^2 r [2r(x-1)]^{n-6}} + \frac{B_{SL}}{\sqrt{3} x^2 r [r(x-1)]^{n-6}}\end{aligned}\quad (13)$$

Since

$$n_1 = \frac{2}{\sqrt{3}(d+2r)^2} = \frac{2}{\sqrt{3} 4r^2 x^2}$$

Hence, when $n = 7$, which is the value deduced using quantum mechanics (10),

$$\sigma - \sigma_L = \frac{1}{x^2 r^2 (x-1)} \left[\frac{3}{32} (B_{ss} - B_{LL} - 2B_{SL}) + \frac{B_{SL}}{\sqrt{3}} \right] \quad (14)$$

Equation 14 suggests that if $1/(x^3 - x^2)$ is plotted against $\sigma - \sigma_L$ a straight line should be obtained. This was indeed found to be true for carbon in paraffin, for which most data were accumulated, except for low values of x , for which the theory must necessarily be inaccurate on account of the large distance between particles and the thickness of the liquid film between them; the consideration merely of pairs of particles is then very inaccurate. The calculated values of $1/(x^3 - x^2)$ taken from the straight line are seen to agree reasonably well with the observed values in table 1.

The value of ρ was calculated from the densities of liquid and solid assuming additivity of volumes. It was found that

$$d(\sigma - \sigma_L)/d[1/(x^3 - x^2)] = 147.1$$

Unfortunately no satisfactory method exists for calculating B_{SL} ; if such a method were available it would be possible to infer the surface energy of the solid. A simple theory which allows only for attractive forces gives

$$\sigma_s = \frac{\pi q^2 \lambda}{(n-1)(n-3)(n-4)(n-5) d_s^{n-5}} = \frac{(n-6)}{2} B_{ss} \frac{1}{d_s^{n-6}}$$

where d_s is the least distance between the centers of *molecules* (1). Antonow's rule clearly does not apply, for if the interfacial surface energy is the difference between the surface energies of the two phases in equilibrium.

the work of adhesion of solid to liquid will be twice the surface energy of the phase of smaller surface energy, which is invariant with respect to the other phase. A method of computing B_{SL} is possible if we follow London and write

$$\lambda_{kl} \propto \alpha_k \alpha_l = I_k I_l / (I_k + I_l)$$

where the α 's are polarizabilities and the I 's characteristic potentials.

With the metallic oxides the analysis is more complex, since the ionic lattice will give a law of force of an exponential nature. However, it is interesting to notice that the slope

$$d(\sigma - \sigma_L)/d[1/(x^3 - x^2)]$$

is considerably greater than for carbon, as would be expected.

The low viscosity of the solvent prevents any considerable aggregation for short times after mixing. Moreover, if aggregation did occur to any considerable extent particles of pure liquid would be left, and the break would occur across these, giving $\sigma = \sigma_L$. A second possible error arises from the penetration of the liquid into the particles. This is not likely to be considerable under the conditions of the experiment, for the particles contain considerable quantities of air before immersion in the liquid. Only the air loosely held between the particles will be removed by the evacuation adopted with the mixture of particles and liquid.

REFERENCES

- (1) BRADLEY: *Phil. Mag.* **11**, 846 (1931).
- (2) BRADLEY: *Phil. Mag.* **13**, 853 (1932).
- (3) BRADLEY: *J. Chem. Soc.* **1936**, 1467, 1799.
- (4) BRADLEY: *Z. Krist.* **A96**, 499 (1937).
- (5) CAWOOD AND PATTERSON: *Trans. Faraday Soc.* **32**, 1084 (1936).
- (6) DERJAGUIN: *Kolloid-Z.* **69**, 155 (1934).
- (7) FOWLER: *Proc. Roy. Soc. (London)* **A159**, 229 (1937).
- (8) HAMAKER: *Rec. trav. chim.* **57**, 61 (1938).
- (9) LENARD: *Ann. Physik* **74**, 381 (1924).
- (10) LONDON: *Trans. Faraday Soc.* **33**, 19 (1937).
- (11) VON ANTROPOFF: *Phil. Mag.* **4**, 273, 792 (1927).
- (12) WASSAJERNA: *Phil. Trans.* **A237**, 105 (1938).

SOAPS AND SIMILAR LONG-CHAIN DERIVATIVES AS SIMPLE HALF-STRONG ELECTROLYTES IN DILUTE SOLUTION

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In the years from 1913 to 1920 we based the existence of colloidal electrolytes upon a comparison of osmotic and conductivity data in solutions of moderate concentration. Very dilute solutions were not studied more especially, on account of the complicating effects of hydrolysis which ordinary soap solutions there display. Our later work, first with Reyckler's cetanesulfonic acid and then with the other more soluble straight-chain sulfonic acids, showed these to be wholly similar to ordinary soap solutions. Moreover, dilute solutions could be studied because hydrolysis is impossible (10).

Our interpretation of soaps as being simple electrolytes in dilute solution, but aggregating with concentration to become colloidal electrolytes, comprising slightly charged molecular aggregates and small but highly charged, and excellently conducting, ionic micelles has long since become familiar. The actual occurrence of the plate-like neutral micelles has been definitely proven by x-ray examination of clear, transparent, alkaline, isotropic, fluid solutions of sodium oleate, whether at rest or streaming (4, 9). Likewise the diffusion data of M. E. Laing McBain¹ clearly necessitate the existence of two kinds of colloid for their explanation.

The formation of ionic micelles was also rendered plausible by the fact that the aggregation of like ions to a larger radial spherical aggregate at once increases the conductivity by several fold and separates these mutually repellent charges on the same ionic micelle to a greater distance apart than they would have occupied as single ions distributed uniformly through the solution, whilst also satisfying the tendency for the paraffin tails of these ions to agglomerate through van der Waals' forces. Such greatly increased conductivity is required to reconcile the fact that in *concentrated* solution the total free sodium ions revealed by the osmotic data would account for only a minor fraction of the actual conductivity, leaving a major fraction due to colloidal anions. These colloidal anions could not, as a comparison of freezing point data with conductivity data requires, carry such enhanced conductivity if they were loaded down either with

¹ Appearing in *Proc. Roy. Soc. (London)* 170 (1939).

added molecules or with ions of opposite charge. Thus, Howell and Robinson (5) well point out that if n univalent spherical ions (of *like* charge) coalesce to form one spherical micelle carrying the n charges, then it follows from Stokes' law that the conductivity of the micelle will be $n^{2/3}$ times as great as that of the sum of the n individual ions. However, they have evidently fallen into error in concluding that a complex ion containing three sodium ions and four anions, with a total negative charge of only one on the univalent complex, will conduct several times faster instead of several times more slowly than a single anion not so loaded.

Recently, however, Hartley (2) and Adam (1), while retaining the concept of colloidal electrolytes as association colloids one of whose conducting constituents is a simple ion, have rejected some of this previous interpretation. They have done this partly by omitting consideration of the osmotic data, that is, the lowering of the freezing point or of vapor pressure, in the restricted region to which the present discussion calls attention.

It is the object of this paper to recall the fundamental validity and inevitability of the comparison of osmotic data with conductivity data in our definitions of crystalloids, electrolytes, and colloidal electrolytes.

Hartley has replaced the constitution diagram of McBain and collaborators in the upper half of figure 1, based upon the necessity of harmonizing freezing point and conductivity, with the freer sketch in the lower half of figure 1, based upon conductivity alone and incompatible with the osmotic data for the region here emphasized.

Figure 1 shows clearly the difference in the predicted lowering of the freezing point in this region necessitated by McBain's diagram in the upper half of the figure as compared with that requisite for Hartley's diagram in the lower half. Taking, for example, the $N/100$ solution, Hartley has practically all the oleate and the greater part of the potassium locked up in colloidal form, leaving only 36 per cent of the potassium ion as the sole depressant of the freezing point. Hence the predicted lowering of the freezing point is $0.36 \times 0.01 \times 1.858^\circ$. On the other hand, the McBain diagram rightly or wrongly represents 51 per cent as simple ions with 44 per cent as simple ion-pairs or molecules, requiring a freezing point lowering of $(0.51 + 0.51 + 0.44) \times 0.01 \times 1.858^\circ$, a value four times greater than that of the Hartley diagram. Although Hartley stipulates that his figure is not strictly drawn, it serves to illustrate the point that there is a contradiction between the two diagrams in their predictions or requirements as to osmotic data in this region. For the same conductivity the upper diagram would require a much greater osmotic effect, which could only be satisfied by osmotically active but non-conducting material such as molecules or simple neutral ion-pairs.

There are four regions of concentration. In the first or most dilute

all agree that the soap is practically completely ionized, and this is shown by both conductivity and osmotic data. Instead of assuming only simple ions, the author considers that at least some ionic micelle is already

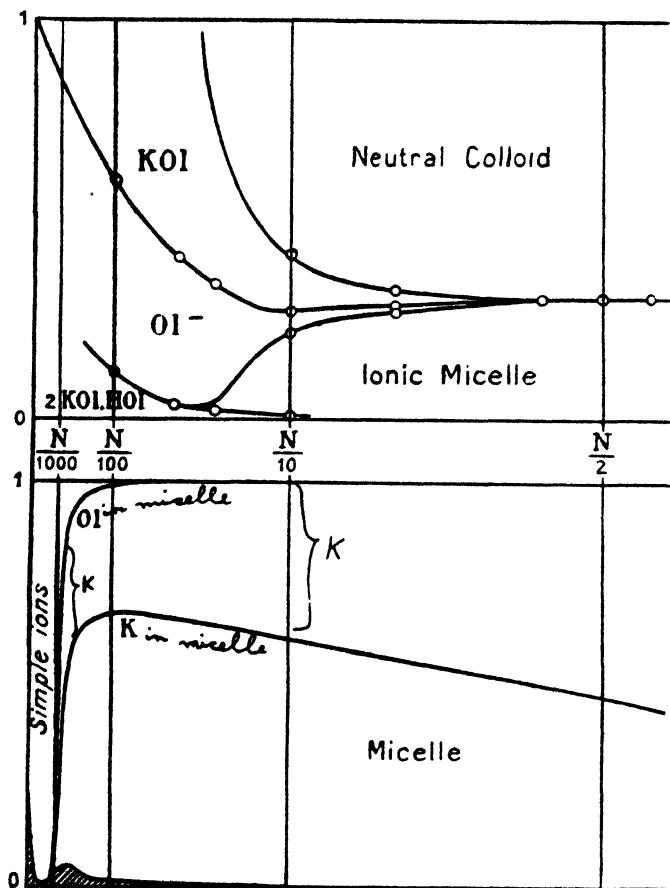


FIG. 1. Constitution diagram for potassium oleate solutions. The upper half of the figure is a diagram of McBain and collaborators. The vertical depth of each field gives the fraction of the oleate ions in the specified form. The lower half of the figure is a diagram (reference 2, page 57, figure 12) drawn by Hartley in accordance with the theory outlined in his book. The vertical depths of the two fields give the fractions of the ions in simple or aggregated form. Line O1 refers to oleate ions and line K to potassium ions. The depth of the shaded area gives the fraction of oleate as covalent acid. Quantitative representation has not been attempted. The annotations in handwriting are by J. W. M.

being formed. In the second region, that discussed in this paper, just after the "critical concentration for micelles" has been reached, the conductivity is falling sharply but the osmotic effects are not falling with corresponding rapidity. Hence in this second region the osmotic effects

are much greater than the conductivity effects, and the difference, as will be seen, can only be accounted for in terms of molecules or simple ion-pairs forming in appreciable amount as a precursor to colloid. In the third region conductivity and osmotic effects both fall rapidly, but the more rapid fall of the osmotic data proves the formation of the colloid, termed neutral colloid by McBain, which conducts poorly as compared with the simple ions and is not uncharged but only relatively poorly charged. In the fourth region both conductivity and osmotic effects, having passed through a minimum, increase strikingly. Now the osmotic effects fall so far *below* the conductivity that McBain found it necessary to postulate the formation of the highly charged, excellently conducting "ionic micelle" in amount steadily increasing in concentration until its properties dominate those of the neutral micelle, which was rather suddenly formed in the second and particularly the third regions. The discussion of osmotic data by Hartley (2, pages 54-56) and Adam (1, page 110) refers only to the third or fourth region and overlooks the second region where colloid is about to form.

Hartley does not recognize the molecules or ion-pairs of the second region. He has unfortunately used, until recently, the term "ionic micelle" for a single kind of colloid particle of changing degree of dissociation or of "electrical neutralization" and intermediate between the ionic micelle and the neutral micelle, but, like the latter, not strikingly different from any charged colloidal particle. His micelle is not that shown by x-rays (4, 9), but is a spherical liquid mass consisting typically of fifty anions and thirty cations with the other twenty cations being free in the surrounding solution.

THE CHARACTERIZATION OF CRYSTALLOIDS AND OF WEAK, STRONG, AND
 HALF-STRONG ELECTROLYTES BY COMPARISON OF OSMOTIC DATA
 (i) WITH CONDUCTIVITY (α)

A crystalloidal non-electrolyte is defined as a substance whose solution exhibits inappreciable conductivity but completely developed osmotic properties. It is convenient to define the osmotic behavior in terms of Bjerrum's osmotic coefficient g , which is 1 minus Lewis and Randall's j or h . Still more convenient for the present purpose is to adopt van't Hoff's single standard i , which for uni-univalent electrolytes is $2g$. For freezing point lowering θ° , $i = \theta/1.858m$, where m is molality or weight normality and 1.858 is the molar freezing point lowering of an ideal non-electrolyte. Similarly, the conductivity may be indicated by α , either the Arrhenius α , the observed molar conductivity divided by that of two completely dissociated ions at infinite dilution, or α_e , the ratio of the observed molar conductivity to that of the fully dissociated ions corrected for interionic attraction and other effects.

Thus a crystalloidal non-electrolyte is defined by $\alpha = 0$, combined with

$i = 1$, within experimental or methodical error. It will be noted that here the presence of simple molecules is recognized by the fact that $i = 1 + \alpha$. Had i been 0.5 instead of 1, we should have postulated double molecules, and had i been a minute fraction of unity, we should have spoken of colloid and not crystalloid.

The chief point to be brought out in this note is that for a partially dissociated substance, if $i = 1 + \alpha$, we are bound to recognize the presence of simple molecules or of their equivalent, simple ion-pairs. The remainder of this communication will be confined exclusively to solutions and regions where $i = 1 + \alpha$, as in acetic acid, dichloroacetic acid, and certain concentrations of soaps and long-chain sulfonic acids where, consequently and necessarily, there is practically no colloid present.

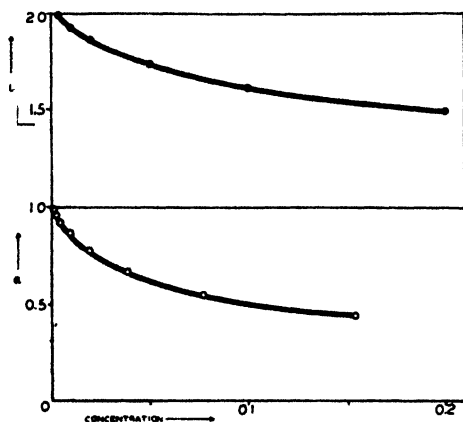


FIG. 2. Relative conductivity (α) and relative freezing point lowering (i) of aqueous dichloroacetic acid, showing $i = 1 + \alpha$.

A typical familiar half-strong electrolyte is dichloroacetic acid. The values of α and i shown in figure 2 are those given in the International Critical Tables (6). The two outstanding characteristics are that over the whole range of concentration α is neither 0 nor 100 per cent and that i is $1 + \alpha$. By no exercise of ingenuity can we reconcile these data with presence of colloid or with absence of simple molecules. This conclusion is especially cogent where α is in the middle of the range such as 60 per cent, and the simple molecules must therefore be recognized as present to the extent of between at least 35 to 40 per cent, or $1 - \alpha$ after the experimental α has been corrected for all possible influences. This follows equally from the value of $i - 2\alpha$ similarly corrected. Any attempt to introduce colloidal particles, whether uncharged, slightly charged, or highly charged, or all varieties together, fails to satisfy both i and α simultaneously, for either i would have to be diminished or α would have to be increased and the spread between them made less than unity. To

replace simple molecules or ion-pairs by colloid of any sort would require that the values of i are in error to the extent of $1 - \alpha$. Dichloroacetic acid is therefore a simple, half-strong electrolyte consisting essentially of the simple molecules and the simple ions. Dissociation is complete in dilute solutions, i being 2 for 0.0025*m*, and α approaching 100 per cent at 0.000012*m*. Corrected for interionic attraction both these values would practically reach their upper limit in distinctly less dilute solutions.

SOAPS AND LONG-CHAIN DERIVATIVES AS SIMPLE PARTIALLY DISSOCIATED ELECTROLYTES IN A LIMITED RANGE OF SOLUTION

It is interesting now to turn to soap solutions *in that restricted, more dilute range* in which, exactly as in the case of dichloroacetic acid, $i = 1 + \alpha$ and where, therefore, we are forced to recognize as appreciable constituents only simple molecules or simple ion-pairs and ions. Instead of simple molecules we may prefer simple neutral ion-pairs of the same formula and weight. These are the regions in such diagrams as that of figure 1, where we had to represent the soaps as being partially dissociated mixtures of simple molecules and simple ions for the cogent reasons just adduced. In still more dilute solutions only ions are left (and in more concentrated ranges colloid enters and soon predominates as shown in figure 1). Discussion of these more concentrated regions will be given elsewhere.

The meagre available data² in this region are given in figures 3 and 4 for potassium hexoate, potassium octoate, potassium decoate, and potassium laurate at 90°C., and for potassium octoate and potassium laurate at 18°C. and 0°C. The dew point method at 90°C. did not allow solutions below 0.2*N* to be measured, and at 0°C. many soaps are either too insoluble or too hydrolyzed for study; a dozen years ago there was no particular interest in making these measurements. The freezing point data at 0°C. are combined with conductivity data at 18°C. or 25°C. Corrections of α and of i for Debye-Hückel effects do not appreciably alter the main point, which is that i exceeds α substantially by unity and also substantially exceeds 2α . The latter balance, like $1 - \alpha$, necessitates the recognition of the presence of a corresponding proportion of simple molecules or ion-pairs.

The data in figure 3 are taken from the lowering of the dew point; those in figure 4 from the lowering of the freezing point, the values $i = 1.56$ and 1.78 for 0.5*m* and 0.25*m* potassium octoate having been obtained by Ts-Ming Woo with a simplified Beckman method.

After viewing figures 2 to 4, it is evident that the McBain diagram in the upper half of figure 1 was drawn by interpolation of the experimental freezing point measurements between the lowest concentration actually

² For references see 7 and especially 11 and 12.

measured and infinite dilution, in conformity with the osmotic data of the other soaps actually measured. On the other hand, Hartley's diagram in the lower half of figure 1 has been drawn speculatively to express a hypothesis, without reference to osmotic data. His diagram requires that the value of i be equal to that fraction of unity lying between the two curves labelled "OI" in micelle and "K" in micelle, this difference being equal to the free potassium ions which are supposed to be the only crystalloidal materials present. Hence his diagram carried the prediction that i is approximately equal to α , instead of being in fact, as in figures 2 to 4, $1 + \alpha$. Imperfect as some of the osmotic data are, this is an impossibly great error to be assumed in any or all of them.

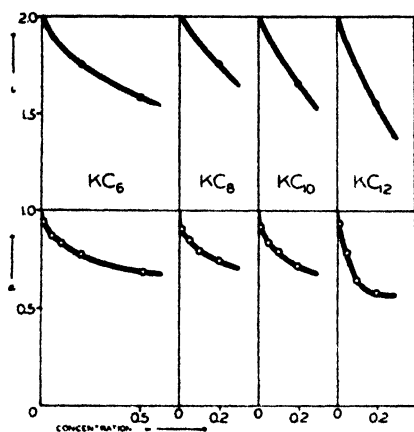


FIG. 3

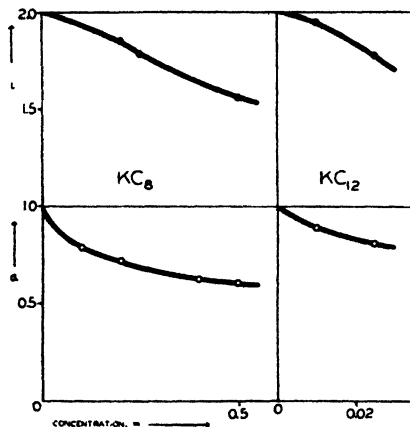


FIG. 4

FIG. 3. Relative conductivity (α) at 90°C. and relative dew point lowering (i) of homologous series of potassium soaps in dilutions where $i = 1 + \alpha$.

FIG. 4. Relative conductivity (α) at 18°C. and relative freezing point lowering (i) of potassium octoate and potassium laurate, in dilutions where $i = 1 + \alpha$.

Soaps behave from the standpoint of ionic strength as uni-univalent electrolytes, as has been shown by the additional conductivity and lowering of freezing point, etc., imparted by other added electrolytes. The charges on the colloidal particles, including those on the ionic micelle, are spaced so far apart that they are practically independent of each other, in accordance with calculations of Simms, Debye, and others.³

The writer considers that even in the most dilute soap solutions there is at least a trace of colloid present, but that this does not exceed a very low percentage until just above the limited region discussed in this communication.

A very few sulfonic acids (8) show in dilute solution the conductivity

³ For data and references see McBain and Searles (13).

expected from the Onsager value, and a few exhibit a still greater conductivity. Moilliet, Collie, Robinson, and Hartley (14) found an apparently normal conductivity for metabenzopurpurin in the first region, although they had shown colloid to be present, and with methylene blue the conductivity in dilute solution rose above its value for infinite dilution. Conductivity alone is therefore no sure criterion.

The point has been raised that sodium salts are otherwise all supposed to be 100 per cent ionized. However, we may remember the uni-univalent salt sodium metaphosphate, which dissolves with very great difficulty in a million or more parts of water, and yet, after being heated to the glassy state, becomes so freely soluble that it is almost miscible with water. However, it is now no longer a uni-univalent salt, but a partly dissociated complex molecule known as Graham's hexametaphosphate or Calgon. In fact there is a whole series of these polymers of sodium metaphosphate and of sodium pyrophosphate, each of which has distinctly different properties, as is shown in selective industrial applications.

SUMMARY

Reëxamination of the experimental evidence obtained for soaps emphasizes the fact that the reinterpretation of colloidal electrolytes recently suggested in several quarters has been based upon a failure to consider, in the region of concentration to which this communication is especially devoted, the osmotic data obtained from experiments on the freezing point and lowering of vapor pressure. The reinterpretation is incompatible with these thermodynamic data, because the osmotic effects are here far *greater* than can be accounted for by colloid and simple ions as deduced from conductivity.

Such solutions are very like those of dichloroacetic acid, and, as in this case, the combination of observed conductivity with observed osmotic measurements proves that simple molecules (or simple neutral ion-pairs of identical formula) and simple ions, and only these, are present in substantial amounts. These precede the formation of neutral micelles. In this range the solutions contain not more than a very slight amount of colloid, probably ionic micelle.

It is pointed out that in much higher concentrations, where aggregation to colloidal electrolytes has occurred and the relation between conductivity and osmotic data is *reversed*, the neutral micelle of McBain and collaborators has been confirmed by x-ray observation, and that this, together with the ionic micelle likewise postulated, is still the most plausible explanation of all the evidence for all concentrations.

REFERENCES

- (1) ADAM: Annual Reports of the Chemical Society (London) **33**, 104 (1936).
- (2) HARTLEY: J. Am. Chem. Soc. **58**, 2347 (1936); "Aqueous Solutions of Paraffin

Chain Salts," *Actualités Scientifiques et Industrielles*, No. 387, Hermann et Cie., Paris (1936).

- (3) HARTLEY: *J. Am. Chem. Soc.* **58**, 2350 (1936).
- (4) HESS AND GUNDERMANN: *Ber.* **70B**, 1800-8 (1937). A private communication from Professor Hess points out that the pH of his solutions was actually 9.5 to 9.8, as determined with the glass electrode, and therefore acid soap was absent.
- (5) HOWELL AND ROBINSON: *Proc. Roy. Soc. (London)* **A155**, 386 (1936).
- (6) *International Critical Tables*, Vol. IV, p. 262; Vol. VI, p. 261. McGraw-Hill Book Co., New York (1928, 1929).
- (7) *International Critical Tables*, Vol. V, p. 445. McGraw-Hill Book Co., New York (1929).
- (8) *International Critical Tables*, Vol. VI, pp. 260-302. McGraw-Hill Book Co., New York (1929).
- (9) KRISHNAMURTI, P.: *Indian J. Phys.* **3**, 307 (1929).
- (10) MCBAIN AND BETZ: *J. Am. Chem. Soc.* **57**, 1905-20 (1935).
- (11) MCBAIN, LAING, AND TITLEY: *J. Chem. Soc.* **115**, 1279-300 (1919).
- (12) MCBAIN AND SALMON: *J. Am. Chem. Soc.* **42**, 426-60 (1920); *Proc. Roy. Soc. (London)* **A97**, 44-62 (1920).
- (13) MCBAIN AND SEARLES: *J. Phys. Chem.* **40**, 493 (1936).
- (14) MOILLIET, COLLIE, ROBINSON, AND HARTLEY: *Trans. Faraday Soc.* **31**, 121 (1935).

SOME OBSERVATIONS ON THE COLLOIDAL IMPURITIES IN DISTILLED WATER

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Apart from the small amounts of electrolytes that are present in distilled water, there are also present small quantities of organic and inorganic colloidal material. For ordinary purposes the latter may be neglected, the specific conductivity being taken as a measure of the degree of purity. When the conductivity is less than 10^{-6} reciprocal ohms, the water is referred to as "conductivity water", and is considered sufficiently pure for most purposes, even the more exacting.

In some few cases, however, this measure of purity is of little value. For instance, in the preparation of colloidal gold by reduction with formaldehyde, traces of certain foreign substances in the water have the effect of preventing the formation of fine-grained stable sols. The action of these substances is unknown, but apparently they slow down the velocity of nuclei formation with the result that crystallization, once it begins, is so rapid that the gold particles become too large to remain in colloidal suspension.

The amount of inhibitory material bears no relation whatsoever to the specific conductivity. Indeed, relatively large amounts of electrolytes are permissible, and actually are present, during the formation of the sol. In spite of this, it is known that certain specific electrolytes are quite harmful, even in small amounts. For example, it has been shown by Zsigmondy and Thiessen (10), Hiege (4), and Reitstötter (9) that the addition of ammonia, hydrazine sulfate, or potassium ferro-, ferri-, or nickelo-cyanide will inhibit the formation of fine-grained sols. More recently, Freundlich and Steiner (3) have shown that the same electrolytes have an inhibitory action on the preparation of colloidal silver.

Furthermore, there is evidence that certain colloidal substances have a similar harmful effect. Zsigmondy and Thiessen (10) have demonstrated the inhibitory action of traces of colloidal silica, which explains the impossibility of purifying water by redistillation through soft glass condensers. Also, in our own laboratories we have found that copper boilers contribute small amounts of colloidal copper oxide, which are decidedly harmful.

As certain amounts of colloidal material are invariably carried over

during distillation, it is possible that the major inhibitory substances in distilled water are colloidal in nature. This view is supported by the results outlined below.

THE STANDARD TEST FOR THE WATER

All samples of water were subjected to a standard test in order to determine whether they would yield fine-grained gold sols with formaldehyde as the reducing agent, the formaldehyde-reduced sol being probably the most sensitive to the retarding influence of traces of inhibitory material. The samples of water which yielded fine-grained homodispersed sols are in this paper referred to as positive, whilst those which failed to yield good sols are called negative.

In order to obtain comparable results, the details of preparation must be rigorously standardized. The method of Cruickshank (1) was adopted, special care being paid to the manner in which the formaldehyde was added, particularly at the instant when the nuclei began to form. The conditions at this instant seem to determine the subsequent stability of the sol.

The usual shaking or swirling was replaced by motor-stirring at constant speed. By standardizing the technique in every detail, it was possible to reveal quite sensitive variations in the water.

THE EFFECT OF FREEZING

It is known that if a solution be frozen and then thawed, the various soluble substances, including the electrolytes, remain in solution, whereas the colloidal material, particularly the hydrophobic, is largely coagulated (2, 7). Experiments were conducted to see if the freezing treatment could be used to throw any light on the nature of the inhibitory substances in distilled water. It was found that, in many cases, negative water could be changed completely to positive simply by freezing and thawing. Owing to the very small amounts of impurities concerned, it proved necessary to observe the following precautions: (1) The water must be slowly frozen from the outside inwards, so that the colloidal material will be gradually concentrated towards the center and there finally coagulated. (2) The frozen solution must be kept at low temperature for at least 24 hr. before thawing, thus making sure that the fine interstitial films have become completely crystalline. (3) Small quantities of water give the best results.

The positive results obtained by this method showed that, in certain cases at least, the inhibitory substances were hydrophobic colloids. In those cases where the water failed to respond, the inhibitory substances may have been electrolytic in character, or, more probably, easily peptized hydrophilic colloids.

THE EFFECT OF STANDING

A low colloid concentration plus an extremely low concentration of electrolyte is in general unfavorable to the stability of hydrophobic sols. From this it would appear that distilled water would gradually improve merely on standing. This proved to be the case. Various samples of water, particularly those which had been distilled from copper boilers (using block tin condensers), were changed from negative to positive by standing in stoppered Pyrex flasks for periods of about two weeks. It so happened that these samples were the ones that gave best results by freezing, but with the latter process the improvement was always more pronounced.

The action that proceeds on standing is not simply a gravimetric precipitation of the larger particles; it is more in the nature of an irreversible coagulation, since the inhibitory substances are not redispersed when the water is shaken.

Again the results point to the presence of hydrophobic colloids.

GRADES OF COLLOID-FREE WATER

It proved desirable to estimate the relative quantities of colloidal material in different samples of distilled water. The "Tyndallmeter" was of no use, since it failed to reach the limits desired, whilst the ultra-microscope revealed but a weak diffused cone with here and there an occasional bright particle, probably dust. The work in this paper concerns itself only with the colloidal material which is harmful to the production of fine-grained gold sols. With this limitation, it is at least possible to assign grades to different samples of positive or negative water, either by ultramicroscopic observation of the size of the reduced gold particles, or more directly by observing the ease of formation of the particles and the particular color of the sol. In this way it becomes possible to speak of the water as having been more or less improved by treatment. For instance, the freezing process invariably improves the water, although it does not necessarily change it completely to positive.

REDISTILLATION

Distilled water can be further freed from both electrolytes and colloidal impurities by redistillation. A second distillation usually produces positive water, so long as extraneous impurities (from the condenser etc.) are excluded. This is the usual method adopted in preparing water for the production of reduced gold sols as used in the Lange test (5), although the technique recently developed by Pennycuik, Woolcock, and Cowan (7) is to be preferred.

Instructions concerning the preparation of gold sols (6) invariably

recommend the use of "freshly distilled" water. This direction is unnecessary, as our results show that distilled water, instead of deteriorating, always improves on keeping. Accordingly the water to be used in the preparation of gold sols, may, and in fact, should, be allowed to stand undisturbed in a stoppered Pyrex container for some weeks before use.

THE ACTION OF STANNIC CHLORIDE

Stannic chloride in acid solution gives rise to tetravalent stannic ions. It also gives rise, by hydrolysis, to small amounts of positively charged colloidal stannic oxide, whose constitution may be represented by $[x\text{SnO}_2 \cdot y\text{SnO}]^{2y+}$. Both the colloidal oxide and the stannic ions are good coagulants of negatively charged colloids.

In weakly basic solution the hydrolysis of stannic chloride proceeds to completion and the colloidal stannic oxide suffers a reversal of charge, being peptized by the free base to form negatively charged particles whose constitution may be represented by $[x\text{SnO}_2 \cdot y\text{SnO}_3]^{2y-}$. Such particles are active coagulants of positively charged colloids.

A series of experiments was carried out to see whether very small amounts of stannic chloride could be used to coagulate the inhibitory material in distilled water, and, if so, to determine the most favorable pH range. This was designed to give some insight into the nature of the charge carried by the inhibitory material.

The results showed that when the pH of the water was kept below 7, the addition of stannic chloride had no effect, but when the pH was adjusted to values above 7, negative water was either markedly improved or else completely converted to positive. Very small amounts of stannic chloride, as small as one part in ten million, were sufficient, the most favorable pH range being from 9.7 to 10.3. Over this range the colloidal stannic oxide is undoubtedly negatively charged, and hence it is evident that the inhibitory material carries a positive charge.

The adjustment of the pH of distilled water by the addition of a little hydrochloric acid or potassium hydroxide may appear anomalous, but it must be pointed out that the water is to be used solely for the preparation of colloidal gold, in which case its pH is always adjusted to about 10 before the addition of the formaldehyde.

An effort was made to obtain some measure of the actual quantity of inhibitory material in a given sample of water by determining the minimum amount of stannic chloride necessary to change the water from negative to positive. When quantities smaller than that stated above (one part in ten million) were used, positive results were often obtained, but the general behavior was variable and unreliable. On the other hand, when larger amounts were used, up to a limit of one part in one million, the results were quite satisfactory. The latter amounts are obviously exces-

sive, and the conclusion may be drawn that negatively charged colloidal stannic oxide does not itself act as an inhibitory colloid.

SUMMARY

Some at least of the substances in distilled water which inhibit the formation of formaldehyde-reduced gold sols are positively charged hydrophobic colloids. Their inhibitory effect can be reduced and sometimes completely removed by (a) allowing the water to stand undisturbed for some weeks, (b) freezing the water, and (c) adding very small amounts of stannic chloride at pH between 9.7 and 10.3.

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REFERENCES

- (1) CRUICKSHANK: Brit. J. Exptl. Path. **1**, 71 (1920).
- (2) EMSLANDER: Der Einfluss des Gefrierens auf Selenhydrosol, p. 21. Dissertation, Stuttgart.
- (3) FREUNDLICH AND STEINER: J. Chem. Soc. **1937**, 1081.
- (4) HIEGE: Z. anorg. Chem. **91**, 145 (1915).
- (5) LANGE: Z. Chemotherap. **1**, 44 (1912).
- (6) MELLANBY AND ANWYL-DAVIES: Brit. J. Exptl. Path. **4**, 132 (1923).
- (7) PENNYCUICK: J. Chem. Soc. **1928**, 2108.
- (8) PENNYCUICK, WOOLCOCK AND COWAN: "The Successful Preparation of Gold Sols for the Lange Test"; in course of publication.
- (9) REITSTÖTTER: Kolloidchem. Beihefte **9**, 222 (1917).
- (10) ZSIGMONDY AND THIESSEN: Das Kolloide Gold Akademische Verlagsgesellschaft m.b.H., Leipzig (1925).

AN X-RAY DIFFRACTION STUDY OF THE SWELLING ACTION OF SEVERAL QUATERNARY AMMONIUM HYDROXIDES ON CELLULOSE FIBERS¹

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Swelling is of fundamental importance in cellulose chemistry, and, as pointed out by Katz (11), one of the most satisfactory experimental methods for studying the intimate mechanism of swelling is by x-ray diffraction analysis. The present investigation was undertaken to obtain more information concerning the swelling action of quaternary ammonium hydroxides on cellulose fibers.

In the present work it was found that certain of the quaternary ammonium bases react to form a "swelling compound" or complex with the crystalline cellulose, as indicated by the appearance of a new x-ray diagram (see figures 2A and 2C). This change in lattice structure is accompanied by a shrinkage of the fiber length and a noticeable increase in fiber diameter, as shown by a comparison of the photomicrographs in figures 1A and 1B. Upon removal of the swelling agent the fiber shrinks in diameter (figure 1C) and the diffraction pattern reverts to that of mercerized or hydrate cellulose (figure 2F).

The quaternary ammonium hydroxides investigated are listed in table 1. The action of these reagents may be divided into three more or less overlapping steps: (a) swelling of the fiber and formation of a complex which gives a new crystalline x-ray diagram, (b) further liquid imbibition during which the fiber continues to swell and the x-ray diagram of the complex is displaced by an amorphous or liquid pattern, and (c) fiber dispersion in the excess reagent. This paper is concerned primarily with the formation and behavior of the quaternary ammonium hydroxide-cellulose complex, as indicated by x-ray diffraction analysis.

Review of literature

The action of quaternary ammonium hydroxides on cellulose appears analogous, in some respects, to that of certain other bases whose swelling compounds with cellulose have been studied with x-rays.

¹ Presented before the Division of Cellulose Chemistry at the Ninety-fifth Meeting of the American Chemical Society, held at Milwaukee, Wisconsin, September 5-9, 1938.

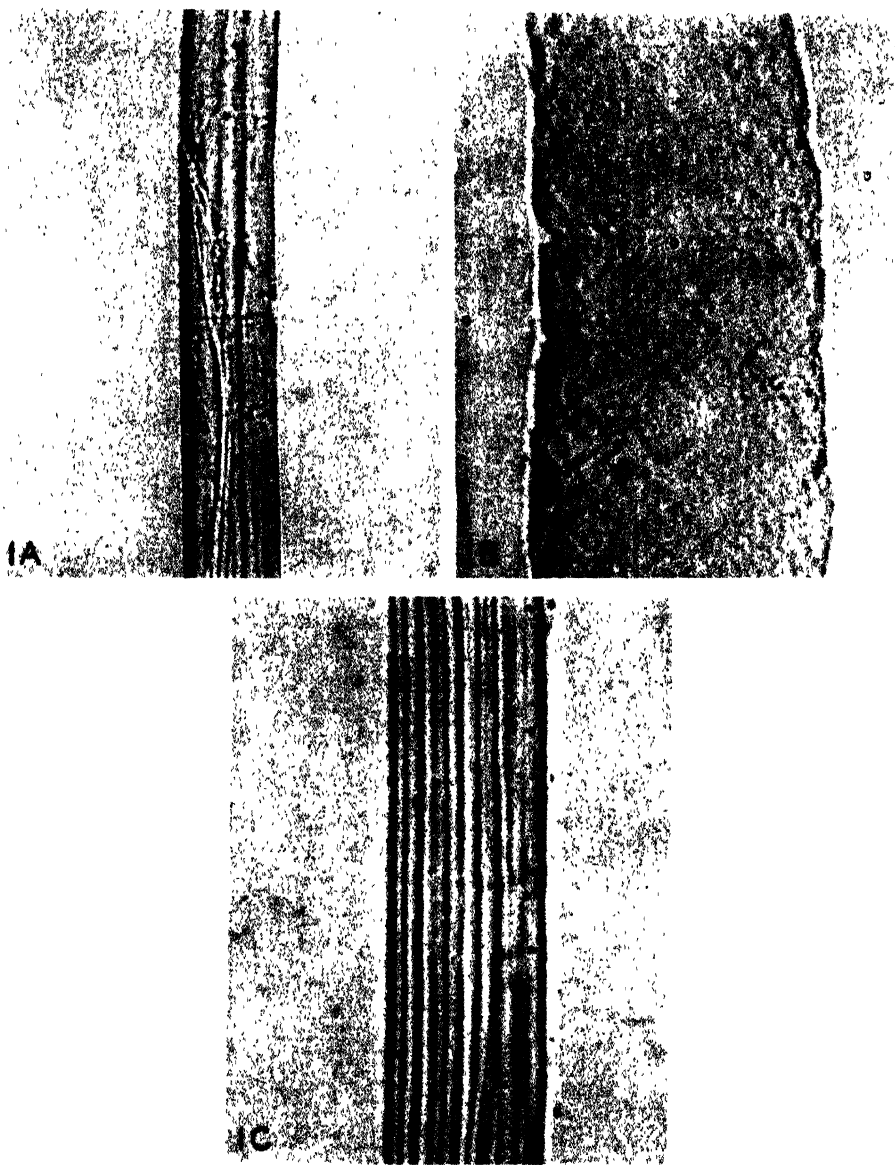


FIG. 1. Photomicrographs of flax fibers showing the swelling action of quaternary ammonium hydroxides ($\times 460$). A. Unswollen fiber. B. Same as figure 1A after swelling in trimethylbenzylammonium hydroxide (swollen fiber structure made visible by adding water). C. Same as figure 1B after removing swelling agent with dilute hydrochloric acid.

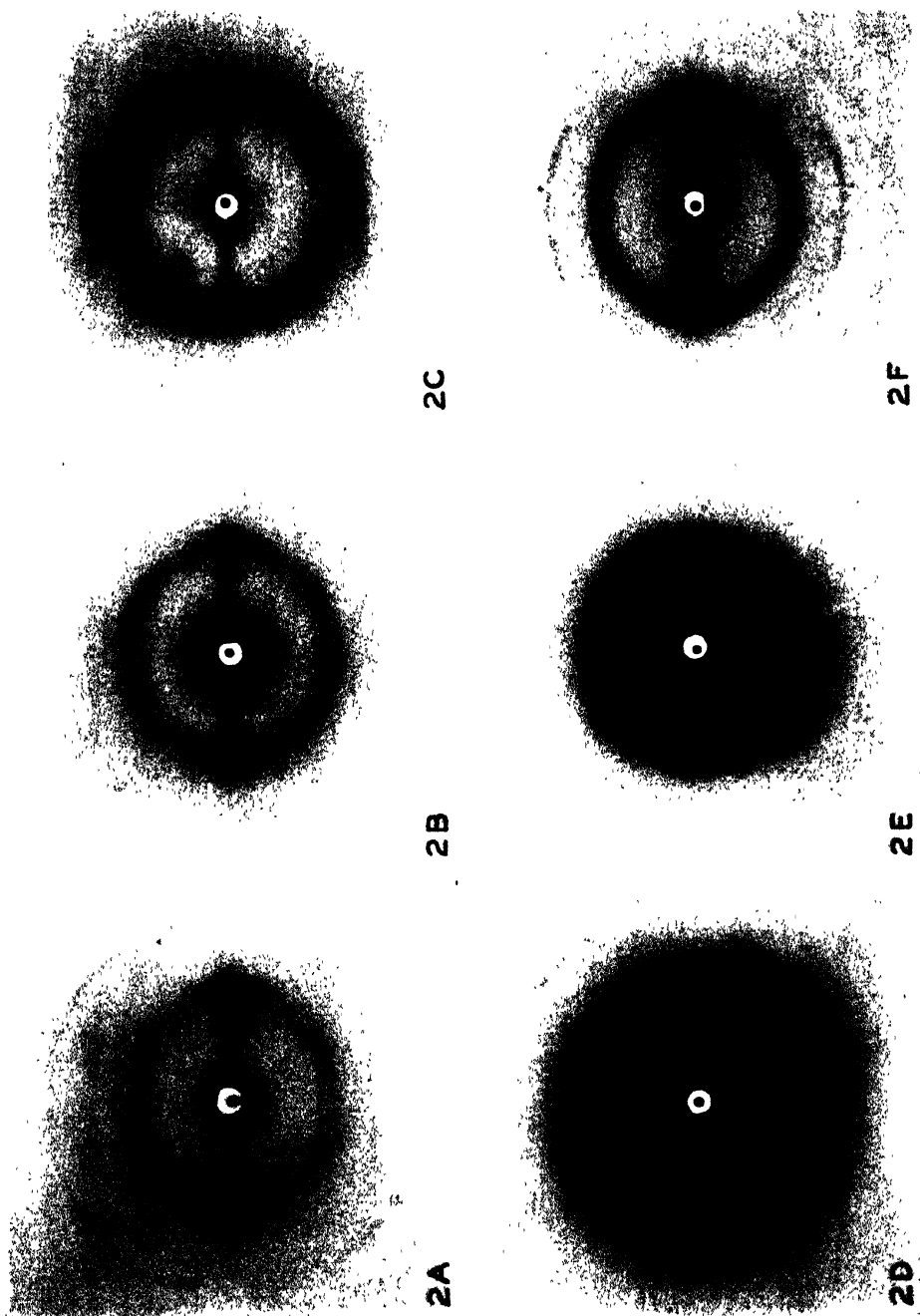


FIG. 2. Diagrams illustrating changes in x-ray diffraction pattern when flax fibers are impregnated with quaternary ammonium hydroxides. A. Native flax fibers before treatment. B. Fibers partially impregnated with tetramethylammonium hydroxide. C. Fibers completely impregnated with tetramethylammonium hydroxide. D. Fibers impregnated with dimethyldibenzylammonium hydroxide. E. Same as figure 2D after being heated for 3 hr. at 100°C. F. Same sample as figure 2E after treatment with dilute hydrochloric acid and washing with water.

The mercerizing action of sodium hydroxide and other alkali hydroxides on cellulose has been known for a long time, and the addition compounds of cellulose and sodium hydroxide (soda-celluloses) have been studied very carefully by many investigators (8, 16). Carbon disulfide has been reported to react with soda-cellulose I during xanthation to form a product that shows a characteristic x-ray diagram (14, 15). Cellulose has also been reported to form two cellulose-copper compounds when swollen with cuprammonium hydroxide (10, 18). In all of the above cases, upon removing the swelling reagent the x-ray diagram reverts to that of mercerized or hydrate cellulose.

Trogus and Hess (19) made a study of the action of aqueous solutions of hydrazine, ethylenediamine, and tetramethylenediamine on cellulose and found that swelling compounds are formed which give definite x-ray diagrams, the nature of which depends on whether native cellulose or mercerized cellulose is used as the starting material. Upon removing the

TABLE I
Quaternary ammonium hydroxides

NAME OF REAGENT	FORMULA	NORMALITY
Tetramethylammonium hydroxide	$N(CH_3)_4OH$	2.0
Trimethylethylammonium hydroxide	$N(CH_3)_3(C_2H_5)OH$	1.9
Trimethylbenzylammonium hydroxide	$N(CH_3)_3(CH_2C_6H_5)OH$	1.6
Dimethyldibenzylammonium hydroxide	$N(CH_3)_2(CH_2C_6H_5)_2OH$	1.15
Choline...	$HO(CH_2)_3NCH_2CH_2OH$	

reagent, x-ray diagrams of the original materials, either native or mercerized cellulose, were obtained. The interaction of cellulose with a series of non-aqueous alkyl amines has been reported by Barry, King, and Peterson (2).

Ammonium hydroxide does not affect the lattice structure of cellulose, but it has been shown by several investigators (3, 5, 7, 9) that liquid ammonia reacts to form an ammonia-cellulose complex. Barry, Peterson, and King (3) found that this complex, upon heating, formed a new modification. Clark and Parker (5) showed the 101 planar extension to be a function of the ammonia content. Hess and coworkers (7) found two further modifications at $-20^\circ C.$ and $-30^\circ C.$

The action of quaternary ammonium hydroxides on cellulose has not heretofore been studied by x-ray diffraction methods. Their fiber-dispersing properties, however, have been discussed by Lieser and Leckzyck (12), and Bock (4) has described a new method of preparing water-soluble cellulose ethers based upon the alkylation of cellulose fibers dispersed in these reagents.

Although all of the above basic reagents are similar in that they form

complexes with crystalline cellulose, as indicated by a new x-ray diagram, they differ greatly in their fiber-swelling and fiber-dispersing properties. In reagents such as the diamines or sodium hydroxide the fiber swelling is limited, while in others, such as cuprammonium hydroxide or the quaternary ammonium hydroxides, swelling continues until the fiber is disrupted and finally dispersed in the reagent. The fiber-dispersing properties of a reagent, therefore, appear to depend not only upon its ability to form a complex, but also upon the mechanism of its swelling action.

MATERIALS AND METHODS

Commercially purified flax fibers in the form of linen thread were used as a source of cellulose in the present investigation, since they gave a well-oriented pattern which agreed well with the data for native cellulose. Kier boiled and bleached ramie and cotton fibers were also used to check the results. The mercerized fibers were prepared by treatment with 18 per cent sodium hydroxide and were then washed and dried. Prior to treatment, the fibers were placed parallel in bundles about 1.5 mm. in diameter, which were kept under slight tension by being clamped in a stretching frame. This simple device is a slight modification of that used by Astbury and Street (1) for stretching wool fibers.

Fibers mounted in this fashion were treated dropwise at room temperature with one of the quaternary ammonium hydroxides, care being taken to impregnate the fibers as uniformly as possible. Usually from four to six drops of base were found sufficient to effect a change in the x-ray diagram. Too much base, especially in the case of dimethyldibenzylammonium hydroxide, was likely to change the fiber material into a gummy mass which no longer gave a distinct fiber pattern. Patterns were taken of the fibers after treatment with the organic bases, after the impregnated fibers had been heated at different temperatures for varying periods of time, and after both the heated and unheated samples were treated with dilute hydrochloric acid and water. Impregnated samples were also allowed to age for several months in order to determine the stability of the compound. As a starting point for the present work, the concentrations of the tetramethyl-, trimethylethyl-, trimethylbenzyl-, and dimethyldibenzyl-ammonium hydroxides were about 33, 36, 40, and 40 per cent, respectively.

X-rays were obtained from a Philips Metalix tube, copper anode, operating at 28 kilovolts and 25 milliamperes. The rays were defined through a pinhole system using 0.020-in. and 0.025-in. pinholes placed 10 cm. apart. In studying the effect of various physical and chemical factors the specimen-to-plate distance was 4 cm. and the length of exposure was from 1½ to 2½ hr. The measurements of interplanar spacings were made with a sample-to-film distance of 9 cm. and a 4-hr. exposure.

Although both products give the same type of x-ray diagram, the term "mercerized" is used to designate fibers treated with sodium hydroxide, while "hydrate" refers to material obtained after removal of the quaternary ammonium hydroxides.

RESULTS

Of the five bases tried (table 1), the tetramethyl-, trimethylethyl-, trimethylbenzyl-, and dimethyldibenzyl-ammonium hydroxides were capable of changing the lattice of both native and mercerized cellulose. Choline, which contains a substituted hydrocarbon group, produced no change in the diffraction pattern of cellulose.

Change in x-ray diagram

The change in x-ray diagram may be divided into three steps. When very little base is added, the pattern is that of either native or mercerized cellulose, depending upon the starting material (figure 2A). At the other extreme, when sufficient base is added, the pattern is that of the modified cellulose complex (figure 2C). Between these two extremes the patterns may indicate the presence of the original cellulose and of the modified cellulose existing together in the same sample (figure 2B). As the new diagram of the swelling compound is formed, that of the original cellulose loses in intensity.

The final x-ray diagram of the quaternary ammonium hydroxide-cellulose complex consists of a crystalline pattern which in most cases is superimposed upon an amorphous pattern. This dual nature of the x-ray diagram apparently arises from the dual structure of the fiber, which consists of cellulose crystallites and an intercrystalline or cementing material. The sharpness of the crystalline pattern of the swelling compound indicates a crystalline structure as well defined as that of the original cellulose. If the fibers are not permitted to shrink perceptibly during impregnation and excess reagent is not added, the orientation of the crystalline pattern may be quite as perfect as that which exists in the original fibers. Since the intensity of the amorphous pattern is related to the amount of reagent added, the pattern probably arises partly from excess reagent in the fiber and partly from the swollen intercrystalline material, which swells indefinitely with the reagent as will be discussed later.

Lattice extension

Table 2 contains the results of measurements from the x-ray diagrams obtained when both native and mercerized cellulose are treated with the various quaternary ammonium hydroxides. For comparison, the measurements of native and mercerized cellulose also are added. It is obvious that the most striking change in the lattice occurs in the distance between

the 101 planes. From a minimum of 6.1 Å. in native cellulose, this equatorial interplanar distance increases to a maximum of approximately 16.7 Å. when native cellulose is treated with dimethyldibenzylammonium hydroxide. This expansion apparently allows room for the introduction of the quaternary ammonium hydroxide molecules in the unit cell.

As the methyl groups of tetramethylammonium hydroxide are replaced by groupings of larger dimensions, there is an increase in the 101 interplanar distance of the corresponding cellulose complexes. By comparing the innermost equatorial spots of figures 2C and 2D, it is apparent that dimethyldibenzylammonium hydroxide produces a greater distention (smaller distance between spots) than tetramethylammonium hydroxide.

TABLE 2
Equatorial interferences

SUBSTANCE	INTERPLANAR DISTANCES IN Å.			
	101 plane		101 plane	002 plane
	Native	Mercerized		
Native cellulose	6.1		5.4	3.95
Mercerized cellulose		7.4	4.45	4.0
Tetramethylammonium hydroxide-cellulose	13.0	12.8	4.0	
Trimethylethylammonium hydroxide-cellulose	13.4	13.0	4.05	
Trimethylbenzylammonium hydroxide-cellulose	16.1	15.8	4.3	4.0
Dimethyldibenzylammonium hydroxide-cellulose	16.7	16.5*	4.4	4.0
Heated modification of dimethyldibenzylammonium hydroxide-cellulose	13.4		4.45	4.2
Heated modification of trimethylbenzylammonium hydroxide-cellulose	13.0		4.5	4.15
Cellulose obtained after removal of swelling agent.	7.5	7.5	4.45	4.0

* This value is approximated, since the compound gives a rather indefinite pattern.

The increase, however, is not always directly proportional to the size of the substituted groups, as, for example, when one of the methyl groups is replaced by an ethyl group. Likewise, within the range of experimental error (± 0.3 Å.), there is not an increase of the 101 planar distance corresponding to the dimensions of an additional benzyl group when the organic base contains two benzyl groups instead of one. These results differ from those obtained by Trogus and Hess (19) on the diamines and by Barry, King, and Peterson (2) on the amines, where the 101 interplanar spacing is directly related to the size of the alkyl group of the entering molecule. The present results may be explained by assuming that the organic base molecules have a definite orientation in the crystal lattice, and that the

second benzyl group in dimethyldibenzylammonium hydroxide does not appreciably increase that dimension of the molecule which arranges itself perpendicular to the 101 plane of the cellulose unit cell.

With each reagent the extension of the 101 plane of native cellulose appears to be slightly larger (about 0.3 Å.) than is the case for mercerized cellulose (see table 2). Here, too, the results differ from those on diamines (19), where the extension of the 101 plane of mercerized is greater than that of native cellulose.

The fiber period as determined from three layer lines is the same for all the compounds studied in the present investigation. The apparent value of 10.3 Å. is identical with that for native cellulose. It is possible, however, that the actual fiber period is some multiple of the value 10.3 Å.

In some of the patterns there are extra spacings (8.0 and 6.3 Å.), which apparently are not associated with the swelling compound. This indicates the existence of another product, such as a modified hydrate cellulose, and suggests the possibility of the compound being in equilibrium with native cellulose and with hydrate cellulose formed by the hydrolysis of the compound.

Effect of concentration

The change in the cellulose lattice is associated with a minimum concentration for each reagent, below which the x-ray diagram of native cellulose is not affected. For tetramethylammonium hydroxide at room temperature this minimum concentration lies between 16 and 20 per cent. For trimethylethyl-, trimethylbenzyl-, and dimethyldibenzyl-ammonium hydroxides the limiting concentrations are 17 to 22, 25 to 29, and 27 to 31 per cent, respectively. These percentages correspond roughly to normalities of 2.0, 1.9, 1.6, and 1.15 (table 1). The normalities of the reagents necessary to change the cellulose lattice decrease linearly when plotted against increasing molecular weights. These results coincide with those of Lieser and Leckzyck (12), who showed that a straight-line curve is obtained if the normality of base necessary to "dissolve cellulose" is plotted against the molecular weight of the base.

The amount of cellulose converted to the swelling compound by the action of a given amount of quaternary ammonium hydroxide appears to be subject to a mass action effect. For example, when a given weight of finely ground native cotton fibers is mixed with a definite amount of a 42 per cent solution of trimethylbenzylammonium hydroxide and allowed to come to equilibrium, approximately 1.5 to 2.0 molecules of base per glucose unit are necessary to effect a complete change in the x-ray diagram. With a 34 per cent solution, each glucose unit requires from 2.0 to 2.5 molecules of base to produce complete conversion. The average value is about 2 molecules of organic base to one glucose unit.

Owing to the presence in the fiber of excess reagent, part of which is held by the swollen intercrystalline material, it is difficult to determine analytically the exact amount of reagent that reacts with the crystalline cellulose to form the quaternary ammonium hydroxide-cellulose complex. An approximate idea of this amount, however, may be obtained from calculations based upon the size of the entering organic base molecule and the increase in volume of the cellulose unit cell. The diameter of the entering quaternary ammonium hydroxide molecule, estimated from interatomic distances, is of the same order as that approximated experimentally by subtracting 7.4 (101 interplanar spacing for mercerized cellulose) from the observed 101 interplanar spacing of the swelling compound. The increase in volume of the unit cell resulting from complex formation may be determined from the data given in table 2. The increase is approximately of the order necessary to accommodate one quaternary ammonium hydroxide molecule per glucose unit. These calculated results are similar to the experimental values obtained by Trogus and Hess (19) on the diamines, in that the ratio of diamine to glucose unit was found to be approximately 1:1.

Preferential action

When a mixture containing equivalent amounts of tetramethylammonium hydroxide and trimethylbenzylammonium hydroxide (or dimethyldibenzylammonium hydroxide) is applied to cellulose fibers, the tetramethyl molecule exerts a preferential action, since the resulting x-ray diagram shows only the interference pattern characteristic of the tetramethylammonium hydroxide-cellulose complex. The explanation for such preferential action is not clear, but it is possible that the molecules of the tetramethyl compound, being smaller than those of either of the benzyl compounds, do not have to expand the cellulose chains so far apart and therefore may enter into the lattice with greater ease. There is the possibility, however, that this preferential action toward the crystalline cellulose may be related inversely to a preferential action of the reagents toward the intercrystalline material. All of the four reagents studied react essentially alike in that they form a swelling compound with the crystalline cellulose, but their action on the intercrystalline material is quite different: the gelatination of the intercrystalline material, as discussed later, is very small with tetramethylammonium hydroxide, but it increases with increasing molecular weight of the quaternary ammonium base, until it is quite pronounced with dimethyldibenzylammonium hydroxide.

The failure of choline to swell the fiber or to produce a change in the diffraction pattern is not explained by the present data, but there is the possibility that it may be related to the polarity of the molecule. Bock

(4) found, in general, "that those quaternary ammonium hydroxides which contain unsubstituted hydrocarbon groups will dissolve cellulose."

Effect of heat

When flax fibers, either native or mercerized, are pretreated with trimethylbenzyl- or dimethyldibenzyl-ammonium hydroxide and then heated at high enough temperatures for a sufficiently long period of time, they tend to shrink and to alter their external appearance. After heating there is obtained a different x-ray pattern, which consists of a new crystalline diagram superimposed upon an amorphous diagram (figure 2E). In the crystalline pattern the 101 interplanar distance is reduced from 16.7 Å. to 13.4 or 13.0 Å. (see table 2). At 50°C. this change takes place within about 15 min., while at lower temperatures more time is required. At room temperature no change in the x-ray diagram occurs even after aging for several months. When the heated samples are treated with trimethylbenzyl- or dimethyldibenzyl-ammonium hydroxide, the 101 interplanar distance increases again to its original dimension of 16.7 Å. Table 2 contains the values of interplanar distances as determined from interference patterns of the heated modifications.

No change in the 101 planar distance could be noted when fibers treated with tetramethylammonium hydroxide and trimethylethylammonium hydroxide were heated for as long as 20 hr. at temperatures as high as 90°C.

Removal of swelling agent

Upon removal of the swelling agent the fibers shrink in diameter, and the x-ray diagram of hydrate cellulose is always obtained regardless of whether the starting material is native or mercerized cellulose. In most cases the swelling agents were removed by treatment with dilute acids, followed by washing with water. The quaternary ammonium hydroxide cellulose complexes differ from those of the diamines in that the latter, after removal of the diamine, yield either native or hydrate cellulose, depending on the nature of the starting material (19).

The modifications obtained by heating cellulose pretreated with trimethylbenzyl- and dimethyldibenzyl-ammonium hydroxides also yield x-ray patterns of hydrate cellulose when treated with dilute acid and water (figure 2F). A comparison of figures 1B and 1C shows the shrinkage in fiber diameter upon removal of the swelling agent.

FIBER SWELLING

Up to this point the discussion has been concerned primarily with the action of the quaternary ammonium bases on the cellulose crystal lattice. The action of these swelling reagents on the fiber as a whole will now be

considered. The fiber-swelling reaction, which proceeds rather rapidly, is characterized by a relatively high rate of diffusion of the base throughout the fiber, as indicated by microscopic examination, and the x-ray pattern indicates an apparently equal modification of all the crystalline cellulose that reacts with the base. This type of reaction, according to Lorand and Georgi (13), is characteristic of the permutoid type. According to Katz (11), the x-ray results are indicative of permutoid intramolecular swelling, accompanied by the formation of a compound of cellulose with the swelling agent, since the change in diagram is not a continuous function of the degree of fiber swelling, and since for each base there is one pattern characteristic of the reacted cellulose. In this case the swelling is in no way explained by the change in x-ray diagram; it is accounted for by the gelatination of the intercrystalline or cementing material, and the permutoid change of the crystal structure of the cellulose is an accessory phenomenon in the mechanism of swelling. In the present paper the term "swelling compound" has been used in the sense described by Katz (11), but the present data do not indicate whether the swelling reaction is identical with the mechanism described by Katz; this is considered by the authors still to be an open question.

From the present data it is clear, however, that the expansion resulting from the formation of the swelling compound accounts for only a small portion of the increase in fiber diameter revealed by microscopic examination. The x-ray patterns show the swelling compound to be formed before appreciable increase in fiber diameter takes place, and, after the swelling compound is formed, further addition of the swelling reagent produces no additional lattice expansion, while the fiber diameter continues to increase. This continued increase in fiber diameter, therefore, is apparently due to swelling of the intercrystalline material. This mechanism is substantiated by microscopic examination, since the fibrils can be observed to be pushed apart and arranged at larger irregular angles to the fiber axis as the fiber diameter increases, while the fibrils themselves appear to remain intact (see figure 1B). The overall swelling reaction, therefore, may be thought of as a dual process; the crystalline cellulose apparently has a limited increase in volume, while the intercrystalline material has no limit. The intercrystalline material may be thought of as forming a true lyophilic colloid, which may swell indefinitely with the dispersion medium, while the crystalline cellulose may be thought of as being lyophobic to the extent that it is not changed beyond the formation of a swelling compound with the reagent. A similar suggestion has been made regarding the swelling of cellulose fibers in cuprammonium hydroxide (17). This dual mechanism of swelling is in agreement with the chemical and slit ultramicroscopic data of Compton (6), which indicate that the cellulose component is not molecularly dispersed in quaternary ammonium bases but rather is dispersed

as cellulose particles. Fiber swelling and compound formation and its relation to fiber dispersion and reactivity are being studied further.

SUMMARY

1. When cellulose fibers, either native or mercerized, are treated with a quaternary ammonium hydroxide, they increase in diameter and give a new x-ray diagram which differs from that of the original cellulose. These results are best explained by assuming the fiber to have a dual structure: the increase in fiber diameter is due to an intercrystalline material which swells indefinitely with the reagent, while the change in x-ray diagram is due to the formation of a swelling compound between the reagent and the crystalline cellulose.

2. The principal change in the x-ray diagram corresponds to a lattice distention of the 101 interplanar distance from 6.1 Å. in native cellulose to approximately 13.0 Å. for the swelling compound between native cellulose and tetramethylammonium hydroxide, and to 16.7 Å. for dimethyldibenzylammonium hydroxide. The fiber period, 10.3 Å., remains unchanged in all compounds.

3. The change in x-ray pattern is not a continuous function of the amount of reagent added, and for each reagent there is one pattern characteristic of the reacted cellulose. This change is associated with a minimum concentration below which the cellulose lattice structure is not changed. Concentration also affects the number of molecules of base per glucose unit necessary to change the x-ray pattern.

4. In mixtures containing equivalent amounts of tetramethylammonium hydroxide and either trimethylbenzyl- or dimethyldibenzyl-ammonium hydroxide the former base exerts a preferential action upon cellulose, the x-ray diagrams being characteristic of the tetramethylammonium hydroxide-cellulose complex.

5. The effect of heat on the swelling compounds of cellulose with trimethylbenzyl- and dimethyldibenzyl-ammonium hydroxides is to decrease the 101 interplanar distance to 13.0 Å. The tetramethylammonium hydroxide-cellulose and the trimethylethylammonium hydroxide-cellulose complexes do not change upon heating.

6. The cellulose complexes from either native or mercerized cellulose or their heated modifications are completely reverted to hydrate cellulose by washing with dilute acid and water.

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REFERENCES

- (1) ASTBURY, W. T., AND STREET, A.: *Trans. Roy. Soc. (London)* **A230**, 75 (1931).
- (2) BARRY, A. J., KING, A. J., AND PETERSON, F. C.: Paper presented before Division of Cellulose Chemistry at the Ninety-second Meeting of the American Chemical Society, held at Pittsburgh, Pennsylvania, September 7-11, 1936.
- (3) BARRY, A. J., PETERSON, F. C., AND KING, A. J.: *J. Am. Chem. Soc.* **58**, 333 (1936).
- (4) BOCK, L. H.: *Ind. Eng. Chem.* **29**, 985 (1937).
- (5) CLARK, G. L., AND PARKER, E. A.: *J. Phys. Chem.* **41**, 777 (1937).
- (6) COMPTON, JACK: *J. Am. Chem. Soc.* **60**, 2823 (1938).
- (7) HESS, K., AND GUNDERMANN, J.: *Ber.* **70B**, 1788 (1937).
- (8) HESS, K., AND TROGUS, C.: *Z. physik. Chem.* **B11**, 381 (1931).
- (9) HESS, K., AND TROGUS, C.: *Ber.* **68B**, 1986 (1935).
- (10) HESS, K., TROGUS, C., LJUBITSCH, N., AND AKIM, L.: *Kolloid-Z.* **51**, 89 (1930).
- (11) KATZ, J. R.: *Trans. Faraday Soc.* **29**, 279 (1933).
- (12) LIESER, T., AND LECKZYCK, E.: *Ann.* **522**, 56 (1936).
- (13) LORAND, E. J., AND GEORGI, E. A.: *J. Am. Chem. Soc.* **59**, 1166 (1937).
- (14) SAKURADA, I., AND FUTINO, K.: *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* **17**, 294 (1932).
- (15) SCHRAMEK, W., AND KÜTTNER, F.: *Kolloid-Beihefte* **42**, 331 (1935).
- (16) SCHRAMEK, W., AND SUCCOLOWSKY, O.: *Kolloid-Z.* **80**, 129 (1937).
- (17) SISSON, WAYNE A.: *Contrib. Boyce Thompson Inst.*, **10**, 113 (1938).
- (18) TROGUS, C., AND HESS, K.: *Z. physik. Chem.* **B6**, 1 (1929).
- (19) TROGUS, C., AND HESS, K.: *Z. physik. Chem.* **B14**, 387 (1931).

MECHANISM OF DEVELOPMENT. I

THE GENERAL EFFECT OF OXIDATION PRODUCTS ON THE DEVELOPMENT PROCESS AND THE NATURE OF THE INDUCTION PERIOD¹

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It is well known that certain developing agents, such as hydroquinone and pyrogallol, show an induction period in their action upon exposed photographic plates, i.e., during the initial stages of development the rate of growth of density increases with the time of action of the developing solution.² Certain other developing agents, such as *p*-phenylenediamine, do not show this behavior. James and Weissberger (6) have recently suggested that a connection might exist between the induction period of hydroquinone development and a catalytic effect of quinone on the development process. It is known that oxidation products of hydroquinone increase the rate of development by that agent. Staude (16) credits R. Luther with the original suggestion. Luther based his conclusions upon the observation of Lüppo-Cramer that development is more rapid in the absence than in the presence of sulfite. This observation is contained, however, in data presented much earlier by Mees and Piper (11). Staude showed experimentally that highly purified hydroquinone dissolved in oxygen-free carbonate solution developed at a much smaller rate than a similar solution having free access to air. In a later paper (17) Staude expressed the opinion that "oxidation products and, above all, the next higher oxidation products of the developing substance play an important part in development. There appears to be a general fundamental principle that a reducing agent is a developer if it has the power of entering even loosely into combination with a pure oxidation product." Staude showed experimentally that development by highly purified hydroquinone solutions is markedly accelerated by oxidation products of hydroquinone, elon, and amidol. He obtained similar results with catechol as developer. All of his work was done with carbonate solutions of pH presumably greater than 10.0, so that it may be questioned whether quinone itself is capable of increasing the rate of development.

¹ Communication No. 707 from the Kodak Research Laboratories.

² See, for example, curves given by Sheppard and Elliott (13).

We have investigated the effect of oxidation products on the rate of development by hydroquinone at lower pH values (8.0 to 8.9) and have extended the investigation to include several classes of developing agents. Our results with hydroquinone, in general, confirm Staude's observations, but further experiments show that an acceleration due to oxidation products is not a general effect for all developing agents, or even for the majority of them. Further, we have shown that quinone catalysis cannot account for the induction period encountered in hydroquinone development. This induction period has its origin in an entirely distinct kinetic phenomenon, involving the penetration by the developer ions of an electrical barrier at the silver halide grains.

EXPERIMENTAL PROCEDURE

The developing agents employed in this investigation were for the most part products of the Eastman Kodak Company and were further purified according to standard procedures. Elonmonosulfonic acid was prepared and purified according to the directions of Tausch (18).

The apparatus employed for development is shown diagrammatically in figure 1. The developing solution was prepared in two parts. The reducing agent was dissolved in water acidulated by the addition of a measured amount of boric acid solution, and the resulting solution was placed in tube A. A measured amount of 0.1 *M* borax (usually 100 ml.) was placed in container B. Purified nitrogen was introduced through the glass tube C, which contained four holes, each with a diameter of 0.072 cm. Nitrogen was passed through the solutions for 1 to 2 hr. at the rate of 200 ml. per minute (at 760 mm. and 20°C.). The solutions were then mixed, allowed to come to temperature, and the film introduced quickly into the solution. The nitrogen flow was continued uninterrupted. The total volume of solution was in most cases 300 ml., although when only limited quantities of developing agent were available a smaller apparatus of 125-ml. capacity was employed. The nitrogen was purified by a method similar to that described by Cameron (3) and failed to give a positive test for oxygen on bubbling through reduced indigodisulfonate for 48 hr. Alkaline hydroquinone solutions prepared as described were perfectly colorless.

The photographic material employed was a normal, unsensitized motion-picture positive silver bromide emulsion of thin and very uniform coating. Exposures were made on the standard Eastman type IIb sensitometer. Each sensitometer strip was split, and the halves were attached to tube D (figure 1) by means of rubber bands.

The time required to remove a strip from the apparatus was 1 sec. Control tests failed to reveal any effect of the air introduced into the apparatus during the removal of the strips. Furthermore, no difference

was obtained when the apparatus was so altered that the sensitometer strips, bound to tube D, were present in tube A during the period of sweeping-out of air, and were introduced into the mixed developer solution by sliding tube D downward through the rubber stopper E. In this case tube B replaced the bubbler F at the top of tube D. Also, no change was noted when the strips were stored for 50 min. in oxygen-free water before development, excepting for a small change in the time of initiation of development by those agents showing induction periods. This change was due to removal of soluble bromide from the film.

Temperature was controlled to within $0.05^{\circ}\text{C}.$ by means of water circulated through the water jacket surrounding tube A. pH determinations were made on the complete solution by means of a calibrated glass elec-

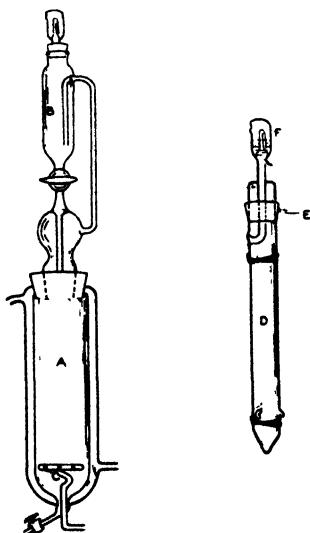


FIG. 1. Development apparatus

trode. Density determinations were made on the Capstaff-Purdy densitometer. Silver determinations were made by potentiometric titration at $70^{\circ}\text{C}.$ with $0.0001\text{ }M$ potassium iodide.

EFFECT OF OXIDATION PRODUCTS

In the case of hydroquinone the primary oxidation product is fairly stable and readily available. The addition of quinone itself, highly purified by successive sublimations, to the pure hydroquinone developer effected a definite increase in the rate of development. This is illustrated in figure 2. The data are for a $0.05\text{ }M$ hydroquinone solution at pH 8.69. Curve I gives the density-time relationship for the pure hydroquinone solution. Curves II, III, and IV are for the same solution except for the

addition of 1/4000, 1/1000, and 1/200 mole of quinone, respectively, per liter. The same relative increase in development rate was obtained at pH 8.29. These results show clearly that the addition of pure quinone to

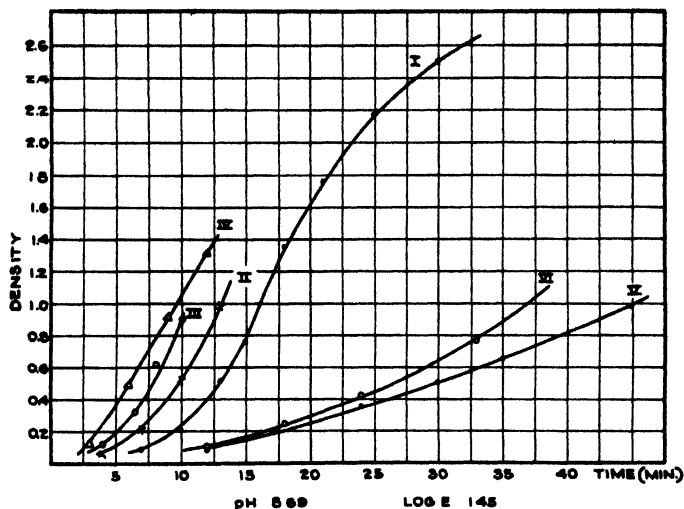


FIG. 2. Effect of addition of quinone to a pure hydroquinone developer

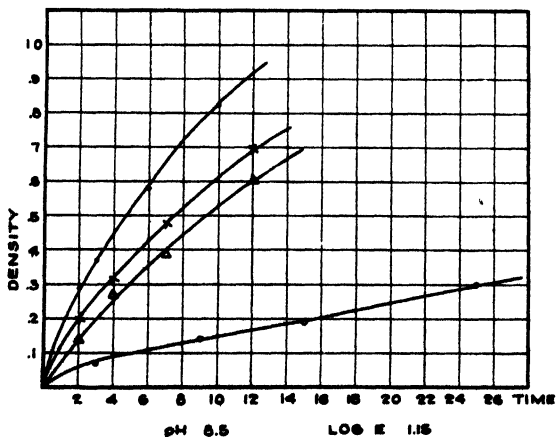


FIG. 3. Effect of sodium sulfite, resorcinol, and 1-naphthol-5-sulfonic acid upon development by 2-amino-5-diethylaminotoluene. O, no addition; X, M/80 sodium sulfite; Δ, M/40 resorcinol; ●, M/40 1-naphthol-5-sulfonic acid.

a pure hydroquinone solution accelerates the developing action of the latter under conditions at which the quinone is reasonably stable. However, some decomposition of quinone will occur during the time required for

development even at pH 8.29, and the possibility still remains that the accelerating effect is due to decomposition products rather than to the quinone itself. The general action of quinone in hydroquinone development will be treated in more detail in a subsequent paper.

Since quinone is formed in the development process, we should expect, from the results just given, that the addition to the hydroquinone solution of agents which rapidly react with quinone would decrease the rate of development. In agreement with this expectation, sodium sulfite and resorcinol definitely decrease the rate of development by hydroquinone. This is illustrated by curves V and VI of figure 2.

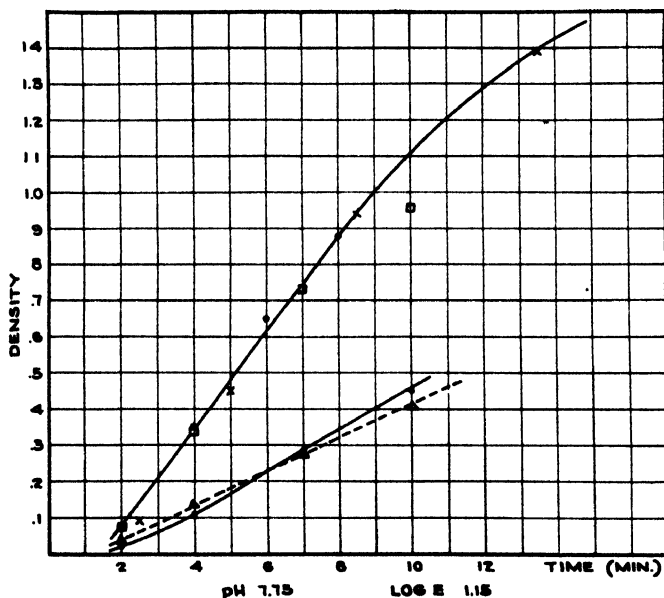


FIG. 4. Effect of sodium sulfite and phenosafranine on development by *p*-aminophenol. ●, no addition; □, *M*/320 sodium sulfite; ○, *M*/80 sodium sulfite; ×, *M*/20 sodium sulfite; Δ, *M*/20,000 phenosafranine.

The accelerating effect that the oxidation products of hydroquinone have upon development by that agent is shown likewise by certain other developers, but is not a general phenomenon. Indeed, in many cases just the opposite effect is obtained. The rate of development by the members of the *p*-phenylenediamine series is, in general, markedly decreased by the presence of the oxidation products, and the same is true of some of the members of the *p*-aminophenol series.

It was not feasible in most cases to study the effect of the oxidation product upon the development rate by direct addition to the developer of pure primary oxidation product, since the latter is, in general, very un-

stable. Instead, we studied the effect of varying quantities of chemicals known to react readily with the oxidation products. Of these sodium sulfite is the most generally useful, although in many cases additional

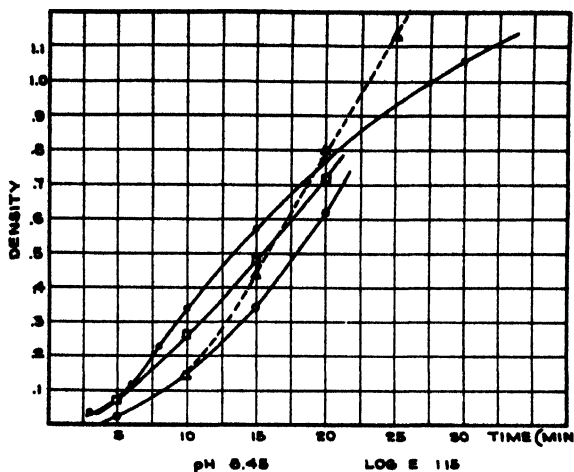


FIG. 5. Development by elonmonosulfonic acid. ●, no addition; □, $M/320$ sodium sulfite; ○, $M/80$ sodium sulfite; Δ, $M/20$ sodium sulfite:

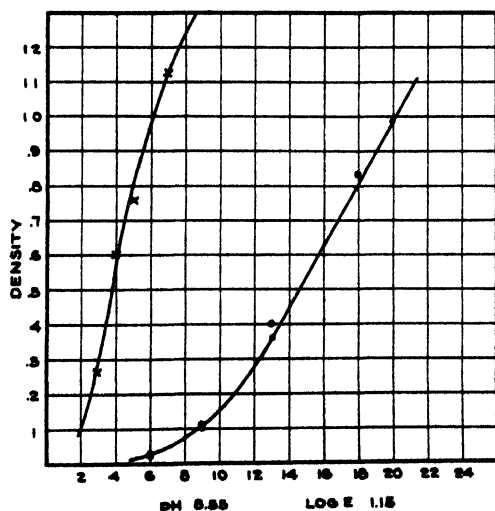


FIG. 6. Development by potassium ferrous oxalate. ●, no addition; ○, $M/80$ sodium sulfite; ×, $M/20,000$ phenosafranine.

"couplers," such as resorcinol and 1-naphthol-5-sulfonic acid, were available for supplementary experiments.

Illustrations of the various types of results obtained are given in figures 3 to 6. The effect of sodium sulfite, resorcinol, and phenosafranine on the

complete list of developing agents tested is given in table 1. The results recorded show conclusively that the effects observed with the coupling agents are due, in major part at least, to their ability to remove the oxidation product. Thus, sodium sulfite markedly increases the rate of development by all members of the *p*-phenylenediamine series *except diaminodurene*, and only in the case of diaminodurene does the sulfite fail to react rapidly with the oxidation product to form a sulfonate. Otherwise, no qualitative difference appears in the development by diaminodurene and the other members of the series. Furthermore, resorcinol markedly increases the rate of development by *p*-aminodimethylaniline, whereas it has no effect upon development by the isomer, *sym*-dimethyl-*p*-phenylenediamine. Resorcinol couples readily with the oxidation product of the

TABLE 1

Effect of sodium sulfite, resorcinol, and phenosafranine upon the rate of development (initial)

DEVELOPING AGENT	EFFECT OF		
	Sulfite	Resorcinol	Phenosafranine
Hydroquinone	Decrease	Decrease	Increase
Pyrogallol	Decrease		Increase
<i>p</i> -Hydroxyphenylglycine	Decrease	None	Increase
Elonmonosulfonic acid	Decrease		Increase
<i>p</i> -Aminophenol	Increase		None or slight increase
Elon	Increase	None	None
<i>p</i> -Aminophenylglycine	Increase		None
<i>p</i> -Aminodimethylaniline	Increase	Increase	
<i>sym</i> -Dimethyl- <i>p</i> -phenylenediamine	Increase	None	None
<i>p</i> -Aminodiethylaniline	Increase	Increase	None
Diaminodurene	None		
Hydroxylamine	None	None	Slight decrease
Potassium ferroöxalate	None	None	Increase

former to form a soluble dye, but the presence of a methyl group on each amino group of the latter agent prevents dye formation. Sodium sulfite, on the other hand, will react readily with the oxidation product of either agent, and it effects a pronounced increase in the rate of development by either. In other cases where action by removal of oxidation products does not appear possible, such as those of hydroxylamine and ferrous oxalate developers, no significant difference was noted between the pure developers and those containing additions of sulfite or resorcinol.

Quantitatively we observe that, beyond a certain small sulfite concentration, further addition of the agent produces little, if any, change in the development rate of elon and *p*-aminophenol. The same is approximately true for elonmonosulfonic acid. This latter compound shows the interest-

ing behavior, however, that sulfite decreases the rate of development in the earlier stages, but that, as development proceeds, the rate eventually becomes greater than that of the solution containing no sulfite (see figure 5). No maximum was reached, however, with the *p*-phenylenediamines tested within the range of sulfite concentrations employed. This is illustrated in figure 7, which gives a portion of the data for *p*-aminodiethylaniline.

The retarding action of oxidation products upon development points to the existence of a reverse reaction tending to destroy the reduced silver. Thus, in the case of *p*-phenylenediamine we can write schematically and

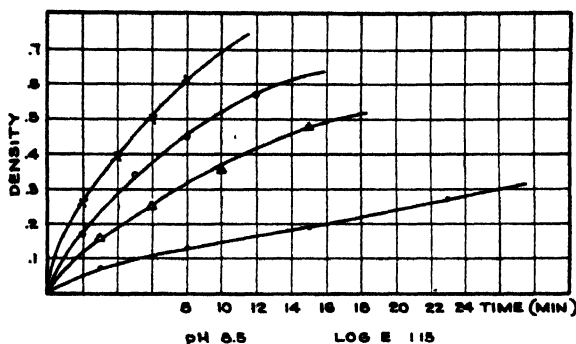
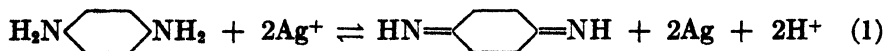


FIG. 7. Curves showing effect of increasing quantities of sulfite on development by *p*-aminodiethylaniline. ●, no addition; Δ, *M*/320 sodium sulfite; ○, *M*/80 sodium sulfite; ×, *M*/20 sodium sulfite.

without reference to the probable two-stage oxidation of the developing agent:



The quinonimine is quite unstable and hence the reaction is not strictly reversible, but the oxidation of silver by the quinonimine may still be rapid enough to compete successfully with the decomposition reaction. The addition of any agent that would decrease the concentration of quinonimine would accordingly act to increase the net rate of development.

The accelerating action of oxidation products on development by certain agents is not so easily explained. A quinone catalysis of the type that James and Weissberger (6) showed to be active in the autoxidation of durohydroquinone and ψ -cumohydroquinone might possibly exist in development. In the heterogeneous development reaction, however, other factors definitely enter, and if a true quinone catalysis exists it may be completely obscured by such factors. In this connection we may cite

the following experimental facts: The autoxidation of diaminodurene shows a pronounced induction period which is removed by addition of duroquinone, just as in the case of durohydroquinone. The rate of oxygen oxidation of other members of the *p*-phenylenediamine series, such as *p*-aminodiethylaniline, is distinctly reduced by the presence of sulfite and coupling agents, such as resorcinol and phenol. However, the addition of quinone to diaminodurene developer results only in a slight *decrease* in development rate, and sulfite and resorcinol markedly *increase* the rate of development by *p*-aminodiethylaniline. Moreover, in the case of hydroquinone itself the effect of quinone is to *decrease* the fogging rate, and that of sulfite or resorcinol to *increase* it. Hence the accelerating effect of quinone upon hydroquinone development itself does not appear to be distinctly an effect upon the reaction between silver ion and hydroquinone. As we shall see later, another explanation of the accelerating action of oxidation products upon development is possible and may be preferable.

These results throw new light upon the problem of the dependence of the rate of development by members of the *p*-phenylenediamine series upon the pH of the solution. The pH dependence observed with the members of the hydroquinone and *p*-aminophenol series may be readily attributed to acid ionization of the hydroxyl groups. A similar explanation, as applied to the *p*-phenylenediamines (4), does not, however, appear reasonable to this writer. Acid ionization of an amino group has been measured only in a few cases, and these measurements have led to fantastically small values. For example, the dissociation constants indicated for aniline and *p*-toluidine (10) are of the order of 10^{-27} . It is hardly conceivable that acid ions could be present in sufficient concentrations at a pH of 8 to 9 to account for the development rate observed with the *p*-phenylenediamines. Certainly, acid ionization plays no rôle in the oxygen oxidation of diaminodurene in the pH range 8 to 11.5, since the rate is independent of the pH in this region.

An alternative explanation of the pH dependence of the *p*-phenylenediamine developers may be based upon the following considerations: We have observed that a decrease in the concentration of the oxidation product results in an increase in the net rate of development. This should be true whether the decrease is accomplished by agents that react with the oxidation product, or by an increase in the alkalinity of the solution which is accompanied by an increase in the rate of spontaneous destruction of the oxidation product.³ This explanation of the increase in rate of development that accompanies increase in pH holds

³ The potentiometric investigations of Fieser, Clark, Michaelis, and others clearly indicate that the stability of the primary oxidation products decreases as the pH increases in the alkaline region.

whether sulfite is present or not, since the marked dependence upon the sulfite concentration shows that, even in the sulfite-containing solutions, the reverse reaction (i.e., oxidation of silver) is occurring to a significant degree. Furthermore, the addition of powerful coupling agents, such as 1-naphthol-5-sulfonic acid, to the sulfite-containing solution increases the development rate. Accordingly, as the pH is increased, the rate of removal of the oxidation product may be increased either by an increase in the rate of spontaneous decomposition or by an increase in the rate of reaction with the sulfite or other coupler.

ORIGIN OF THE INDUCTION PERIOD AND CLASSIFICATION OF DEVELOPERS ACCORDING TO THE CHARGE OF THE ACTIVE PARTICLE

An inspection of the development curves given in figures 2 to 7 shows that with some developers no induction period appears, that with others a short induction period is present, and that with still others the induction period is pronounced. A comparison of the curves obtained for all of the developing agents tested revealed four distinct types. These types are not defined by the chemical nature of the developing agents, but rather by *the charge on the reducing ion or molecule*. In table 2 the developing agents tested are grouped according to the chemical series and to the charge on the actual reducing agent.

Figure 8 gives a comparison of the curves characteristic of each charge group. When the reducing agent is uncharged (group 0), there is no induction period. If the agent possesses a single negative charge (group -1), a small induction period appears. The extent of the induction period increases progressively as we pass to two negative charges (group -2) and to three negative charges (group -3). This behavior was observed with every agent tested, regardless of the chemical series to which the agent belongs. Group 0 contained only members of the *p*-phenylenediamine series which, as we have observed, should not undergo significant acid ionization at the pH employed. Group -1 contains some of the *p*-aminophenols, a *p*-phenylenediamine which has obtained a negative charge by virtue of dissociation of the acid carboxyl group it contains, and the inorganic substance hydroxylamine. Group -2 contains hydroquinone, which, in the pH range employed, is active as the divalent ion, two members of the *p*-aminophenol group which have acquired an added negative charge by virtue of ionization of a carboxyl or sulfonic acid group, and potassium ferroöxalate.⁴ The active ionic species of pyrogallol has not been definitely established as yet, but the curve of the pyro developer fits fairly well into group -2. Group -3 has as its sole representative sodium hydroquinonemonosulfonate.

⁴ This developer had the composition *M*/40 ferrous sulfate, *M*/5 potassium oxalate, and 0.1 g. potassium bromide per liter. The solution was buffered at pH 8.56.

TABLE 2
Classification of developing agents

CHEMICAL SERIES	CHARGE ON ACTIVE PARTICLES			
	0	-1	-2	-3
Hydroquinone			Hydroquinone	Sodium hydroquinonemonosulfonate
<i>p</i> -Aminophenol		Elon <i>p</i> -Aminophenol	<i>p</i> -Hydroxyphenylglycine Elonmonosulfonic acid	
<i>p</i> -Phenylene-diamines	<i>sym</i> -Dimethyl- <i>p</i> -phenylenediamine <i>p</i> -Aminodiethylaniline Diaminodurene 2-Amino-5-diethylaminotoluene	<i>p</i> -Aminophenylglycine		
Others		Hydroxylamine	Pyrogallol ($\text{Fe}(\text{C}_2\text{O}_4)_3^{--}$)	

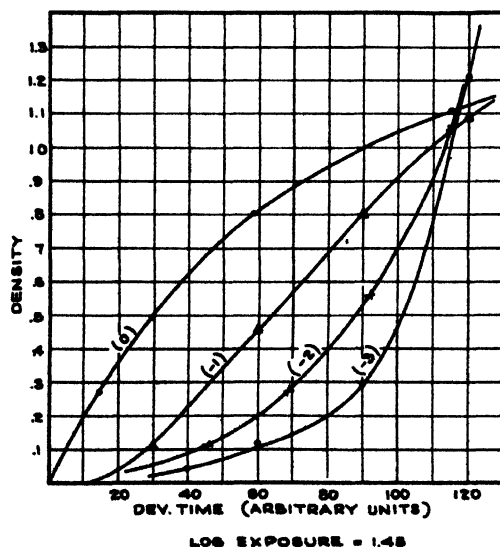


FIG. 8. Effect of charge of reducing agent upon shape of development curve. \times , hydroquinone; Δ , *p*-aminophenol; \bullet , diaminodurene; \circ , sodium hydroquinonemonosulfonate.

It was found that, when conditions were so adjusted that the effect of oxidation products on the rate of development was minimized, the lower portions of the density-time curves for all the agents in group -1 could

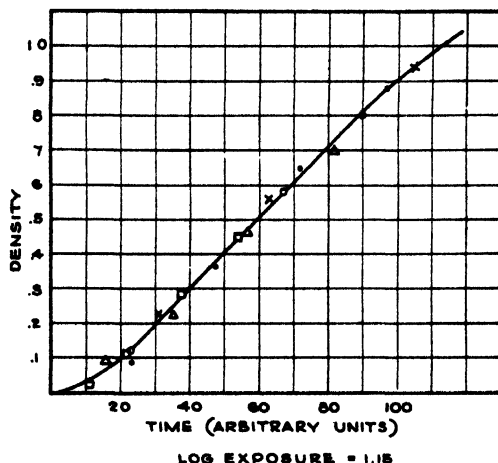


FIG. 9. Induction period of development by monovalent ions. ●, *p*-aminophenol (*M*/80 sodium sulfite); □, *p*-aminophenol (no sulfite); ○, *p*-aminophenylglycine (*M*/80 sodium sulfite); △, hydroxylamine (*M*/80 sodium sulfite); ×, elon (*M*/80 sodium sulfite).

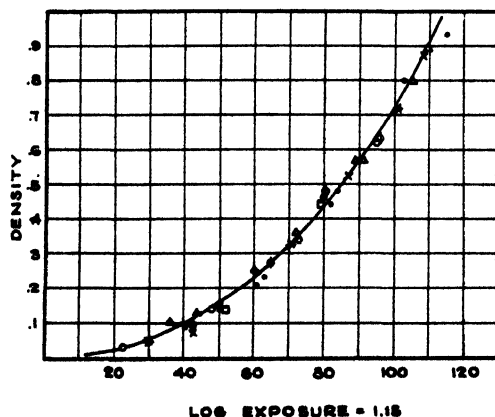


FIG. 10. Induction period of development by divalent ions. ●, hydroquinone; ○, elonmonosulfonic acid (*M*/80 sodium sulfite); □, elonmonosulfonic acid (*M*/20 sodium sulfite); △, *p*-hydroxyphenylglycine; ◊, *p*-hydroxyphenylglycine (*M*/80 sodium sulfite); ×, pyrogallol (*M*/40 sodium sulfite); *, ferrous oxalate.

be superimposed by properly adjusting the time scale to compensate for the difference in absolute development velocities. The same holds true of the agents in group -2. This is illustrated in figures 9 and 10.

The data employed were obtained in the pH range 8.3 to 8.6 in all cases except for elon and hydroxylamine, for which the pH values were 6.6 and 10.25, respectively. Elon was too active and hydroxylamine too inactive for accurate work in the pH range 8.3 to 8.6. In all instances good agreement was obtained in the absence of sulfite when only data for densities lower than 0.4 were used. In the presence of sulfite as a remover of the oxidation product the agreement extended to considerably higher values, and this was true in some cases when sulfite was not employed.

Other kinetic properties fall in line with this classification. The rate of development by every member of group -2 is increased from two- to threefold by the addition of 1/20,000 mole of phenosafranine, whereas little or no effect is produced upon the rate of development by members of groups 0 and -1. The effect of phenosafranine is even more pronounced in the case of sodium hydroquinonemonosulfonate (group -3) where the increase is about sevenfold. Furthermore, the initial rate of development by all members of group -2 except ferrous oxalate is decreased by small amounts of sodium sulfite (removal of oxidation product). None of the members of group 0 or group -1 shows this effect. The action of small additions of potassium bromide upon development by members of group -2 is to increase the induction period markedly without significantly changing the ultimate rate. A similar, but much smaller, increase in induction period is noted with members of group -1. Even large amounts of bromide do not cause the appearance of an induction period with members of group 0.

An explanation of the behavior just described appears from a consideration of the conditions prevailing at the surface of the silver bromide grains. Let us examine first the situation that obtains in a pure silver halide sol. Such a sol readily adsorbs halide ions from the solution. The magnitude of the adsorption, for small halide-ion concentrations, follows the equation:

$$dx = a \cdot d \log c$$

where x is the amount adsorbed, a is a constant, and c is the equilibrium concentration of the ion absorbed (7, 8). As adsorption proceeds, the negative charge on the colloid particles increases. Verwey and Kruyt (20) demonstrated that, in the case of a silver iodide sol in water, the iodide ions are not adsorbed over the entire surface at the maximum, but only at certain active spots on the surface, corresponding probably to cracks and imperfections in the crystal, corners and edges of sub-microscopic crystals, etc. Astakhov and Suzdal'tzeva (1) obtained similar evidence with silver bromide sols (cf. also the data of Fajans (5) on the adsorption of silver ion by silver bromide). The adsorbed ions

on the silver halide surface give rise to a potential drop between the particle and the solution. Smoluchowski (15) assumes a continuous drop in potential in both the solid and liquid phases. Some confirmation of this assumption is supplied by the calculations of Verwey (19) from data obtained with purified, well-aged silver iodide sol, which showed that the potential drop in the rigid and diffuse portions of the double layer (ψ) amounts to only about one-half the thermodynamic potential, and that the drop in the non-rigid portion of the double layer (the ζ -potential) is even less. The remainder of the potential drop is assumed to occur within a thin surface layer of the solid phase.

In the case of silver bromide grains in a photographic emulsion we should expect much the same situation, except that here the layer of gelatin that is tenaciously held by the grain (14) enters as a modifying factor. Bendien (2) has shown that the addition of gelatin to a gold sol (negative) affects the electrophoretic velocity. The negative velocity is decreased by the gelatin in the alkaline region, and the sign is reversed as we pass to the acid side of the isoelectric point of gelatin. This means a decrease or reversal of sign of the calculated ζ -potential of the particles, presumably gold well encased in gelatin. The sign of the potential is, however, always negative when the sol is on the alkaline side of the isoelectric point. The same should apply to the negative silver halide sols. The magnitude of the potential barrier that a negative ion would have to cross in order to reach the silver halide surface may suffer a similar, but no greater, decrease owing to the gelatin. It is probable, however, that the decrease, if any, will be much less. In the normal developing-out emulsion, therefore, we have the silver halide grains protected from the negative developer ions by a negative potential barrier. In the reduction process the developer particles must either penetrate this barrier or the silver ions must pass out to the developer. If the former is the case, the energy that the developer particle must have in order to penetrate this barrier will depend upon the charge on the particle. The magnitude of this potential barrier cannot be determined accurately in the case of the emulsion used in this present investigation, but, by analogy with Verwey's results with silver iodide, it may be inferred that 0.1 volt is a reasonable figure for the ζ -potential. Assuming this as the potential barrier to be crossed, it is seen that a particle of unit charge must possess a kinetic energy equal to or exceeding

$$\frac{0.10}{300} \times 4.80 \times 10^{-10} = 1.6 \times 10^{-13} \text{ ergs}$$

A particle having a double negative charge must possess twice this energy, whereas a particle having a zero charge would not be restrained by the barrier. The energy required by the charged developer particles is

greater than the average energy which they possess (ca. 6×10^{-14} ergs at $20^\circ\text{C}.$) and hence only that fraction which, by virtue of the energy distribution, possesses a kinetic energy equal to or in excess of the critical amount can penetrate the barrier. Since, in the distribution function⁵ the energy term occurs in the exponential, a much smaller fraction of divalent ions will possess the required energy than of monovalent ions, and hence the effective concentration at the surface of the grain will be much smaller.

Now, as development proceeds and the silver area expands, the bromide ions that originally protected the surface will become desorbed, since they are not held to the silver. Hence the potential barrier in this region will become smaller and smaller. Whether or not the barrier will eventually become zero cannot be predicted without a more detailed knowledge of the surface conditions and the development mechanism. As the barrier becomes smaller, however, the fraction of ions possessing sufficient energy to penetrate it will increase, and the relative increase will be greater for divalent than for monovalent ions. Hence, as development progresses the effective concentration of the developer at the surface of the grain increases, and the relative increase will be greater the higher the negative charge on the developer ion.

These considerations just given would predict an induction period in the rate of development of the *individual grain*, provided the developing agent is a negative ion. We cannot assume, however, that in practice we have to deal with an ensemble of identical grains. We must consider that, in reality, the grains of our ensemble vary among themselves in the amount of effective exposure and probably also in the magnitude of the original potential barrier. It is highly probable that the presence of a latent image decreases the magnitude of the original potential barrier, and that the decrease will become greater as the amount of exposure increases. Although developability of an exposed grain cannot be attributed solely to this cause, the barrier effect may markedly influence the relative developability of a series of unequally exposed grains. We cannot determine the conditions existing at each particular grain. We may study the effect of variation in exposure of the individual grains within a given ensemble, however, by comparing the data obtained for several ensembles which have been given different general exposures (i.e., several exposure steps on the sensitometer strip). This type of comparison for hydroquinone developer is given in figure 11. In the construction of this figure a correction was applied, which reduced the experimental densities to give the same value for maximum development of the three exposure steps. Hence the three curves correspond roughly

⁵ Boltzmann function.

to three ensembles, each containing the same number of developable grains, but differing in the average amount of exposure per grain. The curves clearly show that the induction period increases as the exposure decreases. This is in agreement with results obtained by Meidinger (12) in the study of the development of large individual grains. Neither Meidinger's results nor ours, however, seem to justify a sharp division of the development process into the two rate components that he discussed. Since Meidinger employed a heavily bromided elon-hydroquinone developer in his investigation, the potential barrier effect should be large. The rate of development during the very early stages would

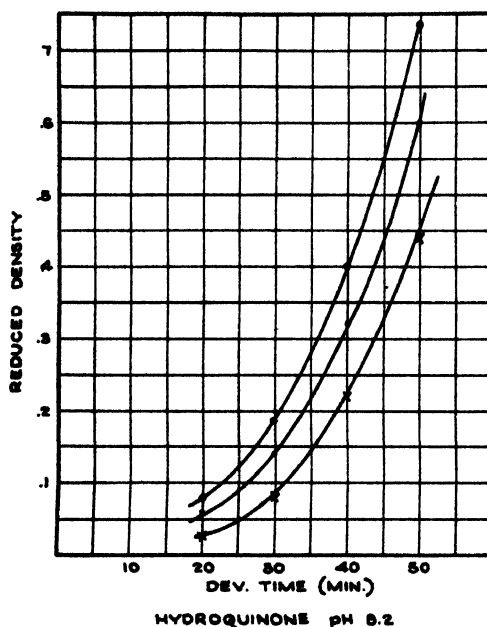


FIG. 11. Variation in induction period with exposure. \circ , $\log E = 1.45$; \bullet , $\log E = 0.85$; \times , $\log E = 0.25$.

depend heavily upon the magnitude of the potential barrier^{*}, and this, in turn, should depend upon the exposure. Before the microscope could detect the "start of development," reduction would have proceeded to the production of several thousand silver atoms, and by this time the potential barrier would probably have fallen to its minimum value at the site of the chemical reaction. Thus we should have a dependence upon exposure of the early part of development, which the microscope could not follow, but no dependence upon exposure of the rate of the part observable through the microscope. The nature of the purely chemical reaction, however, need not change.

A number of otherwise puzzling experimental facts may be explained on the basis of the picture we have presented. Any agent that will reduce the potential barrier will accelerate development by the negative ions in the early stages, whereas an agent that can increase the barrier will have the opposite effect. Thus we can explain the action of small amounts of soluble bromide, which increase the induction period but do not appreciably affect the ultimate rate of development. Larger quantities of bromide probably affect the rate of the chemical reaction itself.

We likewise find a ready explanation for the accelerating effect of neutral salts upon hydroquinone development (9) and the similar action of thallous ion and such basic dyes as pinachrome and pinacyanol. The neutral salts in the concentrations used by Lüppo-Cramer will act to reduce markedly the ζ -potential at the silver halide grains, and hence to decrease the potential barrier. Thallous ion and the basic dyes reduce the ζ -potential by adsorption, and hence will be effective in much smaller concentrations than, say, potassium nitrate. A possible alternative explanation (6), that the action of phenosafranine is one of quinone catalysis, cannot be considered satisfactory. We have observed an accelerating effect of phenosafranine only for the developing agents with di- and trivalent ions (except for a very slight effect on the monovalent ions), and the acceleration is just as pronounced with the ferrous oxalate developer (figure 6) as it is with hydroquinone. Quinone catalysis could hardly be assumed for ferrous oxalate development. The accelerating effect of oxidation products of the developers themselves may be due in a large measure, at least, to their action upon the potential barrier. It is significant that acceleration is observed only among the members of groups -2 and -3, and that every organic member of these groups shows the effect. We shall discuss this question further in a subsequent paper.

An important corollary of the explanation just given of the charge effect in development is that *the chemical reaction itself must take place beyond the potential barrier and hence be localized at or very near the surface of the grain*. This conclusion appears to hold good for the *p*-phenylenediamines as well as for the other agents considered, since the charge effect is quite definitely present in the case of *p*-aminophenyglycine.⁶

It is to be expected that the charge effects that we have described will vary in magnitude from emulsion to emulsion. In emulsions containing a low excess of halide or a large amount of sensitizing dyes, the potential barrier at the grain will be small. An increase in the bromide content of the ion developers will increase the effect. The ferrous oxalate developers

* The alternative possibility, i.e., that silver ions migrate out into the solution and are there reduced, offers no explanation either of the charge effect or of the general kinetics.

should be quite sensitive to free ferrous-ion content.⁷ This may explain the practical absence of an induction period observed when an acid ferrous oxalate developer containing only a slight excess of potassium oxalate is employed. Further, in some of the practical developers, such as D-76, the solvent action of the sulfite probably enters in to a marked extent, and we may no longer assume with safety that the reducing action occurs at the grain surface, at any rate entirely so.

SUMMARY

1. An apparatus and technique are described for the study of photographic development in the absence of oxygen.

2. The presence of an induction period is demonstrated in development by all of the agents tested that possess a negative charge on the active ion. When the uncharged molecule is the active agent, no induction period appears.

3. The magnitude of the induction period increases with the negative charge of the active ion. When the effects of oxidation products upon the course of development are minimized, the curves representing the induction period for agents of any given ion species (-1 , -2) may be superimposed by correcting for the differences in absolute reaction rates.

4. The existence of an induction period in development by negative ions may be explained on the assumption that an ion must penetrate a potential barrier due to adsorbed halide ions before it can effect reduction. This implies that the chemical reaction itself must take place within the potential barrier and hence must be localized at or very near the surface of the grain.

5. The action of phenosafranine, potassium bromide, and neutral salts in high concentrations is shown to be in agreement with predictions based upon the effect of these agents on the ζ -potential of the silver halide grain.

6. Oxidation products of the organic developing agents may act either to increase the rate of development or to decrease it. In general, an increase is observed among the developing agents that are active as divalent ions; a decrease is observed among those active as monovalent ions or neutral molecules.

7. The decrease in development rate due to oxidation products is especially pronounced among the members of the *p*-phenylenediamine series. It is suggested that the increase in development rate that accompanies an increase in pH of the *p*-phenylenediamine solution is due to the accompanying increase in rate of destruction of the oxidation products.

⁷ It is further possible that, in the case of ferrous oxalate, as the developing solution becomes more acid the effective barrier becomes smaller, owing to the effect of pH upon the gelatin.

The author is indebted to Dr. S. E. Sheppard of these Laboratories for valuable discussion and criticism.

REFERENCES

- (1) ASTAKHOV, K. V., AND SUZDAL'TZEVA, M.: J. Phys. Chem. (U.S.S.R.) **6**, 1348 (1935).
- (2) BENDIEN, W. M.: Thesis, Delft, 1926.
- (3) CAMERON, A. E.: J. Phys. Chem. **42**, 629 (1938).
- (4) DE LANGHE, J. E.: De Grondslagen der Fotografie, p. 278. N. V. de Spiegel, Amsterdam (1935).
- (5) FAJANS, K.: Z. physik. Chem. **105**, 255 (1923).
- (6) JAMES, T. H., AND WEISSBERGER, A.: J. Am. Chem. Soc. **60**, 2092 (1938).
- (7) KOLTHOFF, I. M., AND LINGANE, J. J.: J. Am. Chem. Soc. **58**, 1528 (1936).
- (8) LANGE, E., AND BERGER, R.: Z. Elektrochem. **36**, 171, 980 (1930).
- (9) LÜPPO-CRAMER: Kolloid-Z. **15**, 164 (1914).
- (10) McEWEN, W. K.: J. Am. Chem. Soc. **58**, 1124 (1936).
- (11) MEES, C. E. K., AND PIPER, C. W.: Phot. J. **52** (N.S. **36**), 221 (1912).
- (12) MEIDINGER, W.: Physik. Z. **36**, 312 (1925); Phot. Ind. **34**, 1305 (1936).
- (13) SHEPPARD, S. E., AND ELLIOTT, F. A.: Trans. Faraday Soc. **19**, 1 (1923).
- (14) SHEPPARD, S. E., LAMBERT, R. H., AND KEENAN, R. L.: J. Phys. Chem. **36**, 174 (1932).
- (15) SMOLUCHOWSKI, M.: in L. Graetz's Handbuch der Elektrizität und des Magnetismus **2**, 366. Barth, Leipzig (1914).
- (16) STAUDE, H.: Fot. Rundschau **72**, 390 (1935).
- (17) STAUDE, H.: Brit. J. Phot. **83**, 532 (1936).
- (18) TAUSCH, E.: Dissertation, Berlin, 1934.
- (19) VERWEY, E. J. W.: Rec. trav. chim. **53**, 933 (1934).
- (20) VERWEY, E. J. W., AND KRUYT, H. R.: Z. physik. Chem. **A167**, 149 (1933).

ELECTROKINETICS. XXI. ELECTROKINETIC THEORY STREAMING POTENTIAL AND THE ELECTROÖSMOTIC COUNTER EFFECT¹

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INTRODUCTION

In preceding publications of this series (19, 21, 22) it was assumed that the theory of Helmholtz (18) could be applied to streaming potential studies involving organic liquids and various solids. In this paper the justification of such an assumption will be attempted.

Helmholtz (18) postulated that, at certain liquid-solid interfaces, the solid component assumes an electric charge of one sign and the liquid assumes a charge of equal magnitude but of opposite sign. These charges were pictured as being arranged in two adjacent layers, one of which was fixed to the solid and the other of which was in the body of the liquid. The potential assumed to exist between these two layers of opposite charge is known as the electrokinetic or the zeta potential. If the solid is held rigidly and the liquid is forced past it, the liquid will tend to carry its charges with it. This will cause a potential gradient to be set up in the direction of streaming, the magnitude of which will depend upon the rate at which charges are transported by the moving liquid and upon the resistance to the flow of an electric current in the direction opposite to that of the streaming. This potential gradient is known as the streaming potential gradient. The total potential built up in the direction of streaming in this manner is the streaming potential. Helmholtz expressed his theory in mathematical form as follows:

$$H = \frac{P\epsilon\zeta}{4\pi\eta K} \quad (1)$$

¹ Paper No. 1686, Journal Series, Minnesota Agricultural Experiment Station. This paper is greatly condensed from a thesis presented by Max A. Lauffer, Jr., to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1937. The thesis, containing detailed tabular data, is on file in the Library of the University of Minnesota.

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where H is streaming potential, P is pressure of streaming, ϵ is specific inductive capacity of the liquid, ζ is the electrokinetic potential, η is the coefficient of viscosity, and K is the specific conductivity of the liquid. The related phenomena of electroösmosis and electrophoresis were also explained in terms of the Helmholtz double layer theory, and the equations involving zeta were derived for each.

The applicability of the Helmholtz theory, as later modified by Guoy (17) and Briggs (5) and derived by Bikerman (4), to systems composed in part of aqueous solutions of electrolytes has been tested by several means. If this theory is adequate, the zeta potential values for a given interface should be identical when calculated from electrophoretic, electroösmotic, and streaming potential measurements. Saxen (Briggs (5, 7)) showed that, if zeta from streaming potential is the same as that from electroösmosis,

$$\frac{\text{electroösmotic velocity}}{\text{current}} \quad \text{is equal to} \quad \frac{\text{streaming potential}}{\text{pressure}}$$

a relationship which he found to hold approximately for a clay diaphragm and solutions of electrolytes. Briggs (6, 7) measured the zeta potential of protein adsorbed on quartz powder against electrolytes at various pH values by the streaming potential method. The values obtained agree only fairly well with those obtained cataphoretically on a similar system by Abramson (1) and on an identical one by Abramson and Grossman (3). Bull (10) determined the zeta potentials of Pyrex glass coated with egg albumin and Bacto peptone in contact with solutions of the respective proteins at various values of pH, using streaming potential, electroösmotic, and electrophoretic measurements. The results of a large number of determinations indicate that the values of zeta calculated from the three types of data are identical. Monaghan, White, and Urban (23) found identical isoelectric points for gelatin on Pyrex glass (pH of 4.75) by streaming potential, cataphoresis, and electroösmosis. DuBois and Roberts (14) measured both streaming potentials and electroösmotic velocities through a glass slit of known dimensions. Using 10^{-3} normal electrolytes, they found that electroösmotic and streaming potential studies gave the same value for the zeta potential. Moyer and Abramson (25) found agreement between electroösmotic and electrophoretic studies on several protein-coated surfaces, even in very dilute solutions of electrolytes, and Moyer (24) found the same relationship to hold for very dilute solutions of protein even in the absence of electrolytes. In spite of the inconclusive nature of many of the earlier studies on this question, this more recent evidence leads to the conclusion that at interfaces, one of whose phases is an aqueous solution of electrolytes, the value calculated for the electrokinetic potential is independent of the method of evaluating.

Another method of testing the validity of the theory of Helmholtz as applied to streaming potential is to observe whether or not the streaming potential-streaming pressure ratio is a constant for a given system for all values of pressure (see equation 1). Ettisch and Zwanzig (15, 16) found an increase in this ratio for increasing values of streaming pressure. Bull (9) repeated their work and found the ratio to be constant in most cases. Even in those few cases in which Bull found the ratio to vary, the potential was a linear function of the pressure. Furthermore, Bull and Gortner (11) found the potential-pressure ratio to be constant for $10^{-4} N$ sodium chloride in a cellulose diaphragm. It would seem that this second test of Helmholtz's theory yields favorable conclusions.

Unfortunately, there are no data on the identity of zeta potentials calculated from cataphoretic, electroosmotic, and streaming potential measurements for systems composed of purified organic liquids and solids. However, some data on pressure-potential ratios are available. Although Martin and Gortner (22) reported that streaming potential-pressure ratios were not constants in various alcohol-cellulose systems, Lauffer and Gortner (21) have recently pointed out that the data of Martin and Gortner show that the streaming potential is a linear function of the streaming pressure. Constancy of potential-pressure ratios demands that streaming potential-pressure graphs not only be straight lines, but also that they pass through the origin of coördinates. It was suggested (21) that the lines obtained by plotting these data failed to pass through the origin because the potentials recorded represented streaming potentials increased or diminished by constant potentials originating elsewhere in the electrical circuit. Jensen and Gortner (19) found pressure-potential ratios to be constant for several acid-aluminum oxide and ester-aluminum oxide systems, and Lauffer and Gortner (21) found further that these ratios were constants in a considerable number of alcohol-aluminum oxide, organic acid-cellulose, and ester-cellulose systems. It is seen, then, that one essential requirement of the double layer theory of Helmholtz is fulfilled by organic liquid-solid systems.

Bikerman (4) has recently derived an equation for streaming potential, taking into account the diffuse double layer theory of Guoy (17). His equation, somewhat simplified, is

$$H = \frac{Pe\zeta}{2\pi L(K + K_s)} \left(\frac{L}{2} - \frac{1}{\alpha} \right)$$

where K_s is the specific conductivity of the surface, α is the reciprocal of the mean thickness of the double layer, L is the radius of the capillary, and the other terms have the same meaning as before. When the capillary radius is large compared to the thickness of the double layer (αL is great), this equation reduces to that of Helmholtz, as modified by Briggs (5).

This question of capillary radius, as related to streaming potential, has recently been the subject of much discussion. The potentials derived by streaming liquids through very small pores have been studied by White, Urban, and Krick (28) and by White, Monaghan, and Urban (29). They found that the streaming potential-pressure ratio decreases with decreasing capillary diameter. This they believed to be due to increased surface conductivity in small capillaries. Bull (8), Reichardt (27), Komagata (20), Bull and Moyer (13), and Moyer and Bull (26) have discussed the measurement of streaming potentials in small capillaries from a theoretical point of view. In this connection there appear to be three factors that must be considered. The streaming potential equation of Helmholtz and Smoluchowski is derived by considering the double layer as being made up of two parallel plates. Actually it consists of two coaxial cylinders. When the radii of the cylinders are small compared to the differences in radii, a large error results, owing to this consideration. Furthermore, in very small capillaries there is an increase in viscosity, dependent upon the radius. This effect becomes pronounced in pores smaller than 10^{-5} cm. Finally, there is the effect of electroosmotic counter pressure, which, according to the treatment of Bull (8), is regarded as being a function of capillary size, specific conductivity, and electric moment of the double layer. It is with the consideration of this effect that the experimental portion of this paper is concerned.

EXPERIMENTAL

In the pursuit of the study previously reported by the authors (21) an important innovation in experimental technique was employed. It will be remembered that the streaming potential for any system is inversely proportional to the specific conductivity of the system (see equation 1). Many of the organic liquid systems studied have very low conductivities, and therefore the streaming potentials are very high. Two experimental difficulties are encountered in such systems: (1) the accurate measurement of the very low conductivities and (2) the measurement of the high values of streaming potential. In order to obviate these difficulties, a short circuit of greater conductivity (about 10^{-7} ohms⁻¹) was placed across the terminals of each of the streaming potential systems. It will be shown in the discussion that, as a natural consequence of the simple theory for streaming potential, this simplification of experimental method should not alter the value of the electrokinetic functions calculated for the several systems. In order to test the theory, streaming potentials were measured on both shunted and unshunted cells for several ester-cellulose systems. Ester systems were chosen for this test because their conductivities in the diaphragms are considerably lower than that of the shunt, but high enough to be measured with confidence. The conductivities of the organic acid

systems used in the previous study were too low to be measured reproducibly, whereas the alcohol-aluminum oxide systems included in that work had conductivities of the same order of magnitude as that of the shunt, and hence were useless as a test of the theory.

The details of the experimental procedure, as well as a discussion of the electrokinetic functions calculated from the data, are found in the previous publication (21).

PRESENTATION AND DISCUSSION OF DATA

In a given diaphragm the rate at which charges are carried by the streaming liquid to the receiving electrode is determined by the rate of flow of the liquid through the diaphragm. The rate of flow is proportional to pressure. Therefore the current that must be conducted from the receiving electrode to the other one at the equilibrium potential is directly proportional to the effective streaming pressure. Since $H = RI$, where H is the potential, R is the resistance, and I is the rate of flow of electric current, $H = CRP$, where C is a proportionality factor and P is the streaming pressure. Therefore $H/RP = C$, or, where K is the conductivity between the electrodes, $HK/P = C$ for any given diaphragm-liquid system, *regardless of the value of the conductivity between the electrodes*. Therefore $HK/P = H'K'/P'$, where H is the streaming potential generated by streaming a liquid under an effective pressure P through a diaphragm of conductivity K , and H' and P' are the streaming potential and the effective streaming pressure for the same diaphragm, the electrodes of which have been shunted through a resistor whose conductivity is K' (K' is much greater than K).

In the equation,

$$q.d. = \eta HK_s/P \quad (2)$$

K_s is the *specific* conductivity of the liquid in the diaphragm. Letting A represent the cell constant, the equation becomes

$$q.d. = \eta HKA/P = \eta H'K'A/P' = \eta H'K_s'/P'$$

Therefore, one should be entirely justified in measuring the electrokinetic function $q.d.$ in a cell whose electrodes are shunted through a known resistance, low compared to that of the diaphragm itself. Indeed, as long as the conductivity of the system, shunt in parallel with diaphragm, is known, no restrictions other than practical ones are imposed upon the magnitude of the conductivity of the shunt that should be used. It should be emphasized that the value of the cell constant must be measured, even though a shunt is used across the terminals of the diaphragm. This does not appear to be unreasonable when one realizes that the cell constant is really a measure of the dimensions of the diaphragm, and hence of the

TABLE I
Data for ester-cellulose systems

ESTER	TREATMENT	K_s ohm^{-1}	$\eta \times 1000$	H/P milliohms per cm. of Hg	$q.d. \times 10^3$ B.S.U. per cm.	$\log \frac{K_s}{(q.d.)^2}$ C.G.S. units	$\frac{P_s}{P}$
Methyl acetate.....	{ No shunt 11-megohm shunt	3.41×10^{-8}	3.44	48.8	13.00		0.0480
		3.07×10^{-7}	3.44	56.9	(13.65)'		0.000
Ethyl acetate.....	{ Diaphragm a Diaphragm b b with 100-megohm shunt b with 50-megohm shunt b with 11-megohm shunt b with 1-megohm shunt	2.69×10^{-10}	4.01	1.76×10^4	4.30	10.471	0.248
		8.50×10^{-10}	4.01	6.56×10^3	5.07	10.971	0.113
		2.86×10^{-8}	4.01	218.1	5.67	12.498	0.009
		6.01×10^{-8}	4.01	104.7	5.71	12.821	0.001
		2.59×10^{-7}	4.01	24.3	(5.72)'	13.455	0.000
		2.94×10^{-8}	4.01	2.375	6.34	14.511	-0.110
n-Propyl acetate.....	{ No shunt 11-megohm shunt	1.305×10^{-10}	5.13	1.91×10^4	2.90		0.073
		2.45×10^{-7}	5.13	11.05	(3.13)'		0.000
n-Butyl acetate.....	{ No shunt 11-megohm shunt	9.55×10^{-11}	6.58	1.68×10^4	2.39		0.350
		2.30×10^{-7}	6.58	10.7	(3.67)'		0.000
n-Amyl acetate.....	{ No shunt 11-megohm shunt	3.86×10^{-11}	7.57	2.575×10^4	1.70		0.190
		2.38×10^{-7}	7.57	5.17	(2.10)'		0.000
Ethyl formate.....	{ No shunt 11-megohm shunt	5.06×10^{-8}	3.75	237	10.19		0.136
		2.85×10^{-7}	3.75	48.7	(11.30)'		0.000
Ethyl propionate.....	{ No shunt 11-megohm shunt	2.09×10^{-10}	4.73	1.245×10^4	2.79		0.076
		2.44×10^{-7}	4.73	11.51	(3.02)'		0.000
Ethyl n-butyrate.....	{ No shunt 11-megohm shunt	3.22×10^{-11}	6.04	5.45×10^4	2.39		0.162
		2.36×10^{-7}	6.04	8.80	(2.85)'		0.000

number of charges that can be carried to one electrode at a given pressure. Therefore, in order to be able to obtain comparable results from one diaphragm to another for the same system, the cell constant must be measured.

In table 1 we find a comparison of the values of $q.d.$ measured with no shunt with those of $(q.d.)'$ measured while using the 11-megohm shunt for a series of ester-cellulose systems. Instead of $q.d.$ being equal to $(q.d.)'$ for each ester system, as our reasoning would lead us to expect, $(q.d.)'$ is actually greater than $q.d.$ in every case.

Abramson (2) and Bull (8) pointed out independently that, when a potential is generated across the ends of a diaphragm by streaming a liquid through it, an electroösmotic counter pressure is set up, which tends to cause liquid to flow in the direction opposite to that of the applied pressure.³ In other words, there is a tendency for the effective streaming pressure to be less than the pressure imposed across the diaphragm. This effect is proportional to the potential drop across the diaphragm and hence, for a fixed applied pressure, should be greater when no shunt is placed across the ends of the diaphragm than it is when the electrodes of the same diaphragm are shunted. In other words, on the unshunted cell the applied pressure overestimates the effective streaming pressure more than it does on the shunted cell, and therefore $q.d.$ is underestimated to a greater extent than $(q.d.)'$. Hence $(q.d.)'$ should be expected to be greater than $q.d.$ for all systems.

Following the method of Bull, this subject may be treated mathematically for the case of a capillary in the following manner:

$$P_s = P - P_e$$

where P_s is the effective streaming pressure, P is the applied streaming pressure, and P_e is the electroösmotic back pressure. From the equation for streaming potential,

$$P_s = \eta HK_s / q.d. \quad (3)$$

and from the equation for electroösmosis,

$$P_e = 8Hq.d./r^2 \quad (4)$$

where r is the radius of the capillary. Combining these three equations, we get

$$P = \eta HK_s / q.d. + 8Hq.d./r^2$$

Dividing by P_s this becomes

$$P/P_s = \eta K_s r^2 / 8(q.d.)^2 + 1 \quad (5)$$

³ Bull considered the electroösmotic counter effect in relation to the error it would cause in the measurement of the streaming potentials in systems with small capillaries, whereas Abramson, proceeding in an essentially identical manner, was concerned with an explanation for the anomalous viscosities shown by very dilute solutions of electrolytes.

From this equation it is apparent that, for systems in which K_s and r are small and $q.d.$ is large, the electroösmotic back pressure effect becomes appreciable, but when K_s or r is large, or $q.d.$ small, this effect vanishes. For fixed values of r and $q.d.$ the back pressure effect becomes important with very small values of K_s , but vanishes when K_s is increased sufficiently.

Data for several studies on the system ethyl acetate-cellulose are summarized in table 1. The first two values of $q.d.$ for this system were measured on unshunted ethyl acetate-cellulose diaphragms of different conductivities. The other values were obtained by making measurements on the second diaphragm shunted through 100-, 50-, 11-, and 1-megohm resistors. Let us assume that the value of $q.d.$ measured using the 11-megohm resistor as a shunt is the true value for $q.d.$ for any system, ethyl acetate-cellulose, and that all smaller values of $q.d.$ for this system are due to deviations resulting from electroösmotic back pressure. We shall designate this value of $q.d.$ by the symbol $(q.d.)'$. Then $(q.d.)'$ is the real value of the electric moment and is given by the expression

$$(q.d.)' = \eta HK_s / (P - P_e)$$

remembering that P_e is assumed to be negligible in the diaphragm shunted through 11 megohms. The apparent value for the electric moment is given by the equation

$$q.d. = \eta HK_s / P$$

With any given diaphragm for a fixed value of P ,

$$q.d. / (q.d.)' = (P - P_e) / P = 1 - \frac{P_e}{P}$$

Hence from the ratio of $q.d.$, calculated for any ethyl acetate-cellulose system, to $(q.d.)'$, the value calculated for the diaphragm shunted through 11 megohms, we can calculate the ratio (P_e/P) of the electroösmotic back pressure to the applied pressure. Values of that ratio are tabulated in table 1. The log of $\eta K_s / (q.d.)'^2$ for each ethyl acetate-cellulose system is readily calculated from the data found in table 1. These values also appear in the table. In figure 1 we find P_e/P plotted against $\log \frac{\eta K_s}{(q.d.)'^2}$ for the studies on ethyl acetate. The points represent values calculated in the manner just described, and the smooth curve is the theoretical curve of figure 2, which has been displaced along the horizontal axis.

Figure 2 shows the theoretical relationship of P_e/P to

$$\log \frac{\eta K_s r^2}{8(q.d.)'^2}$$

It was plotted by assigning arbitrary values to the latter expression and calculating P_e/P by substituting this into equation 5. The horizontal displacement of the theoretical curve necessary to make it fit the points of

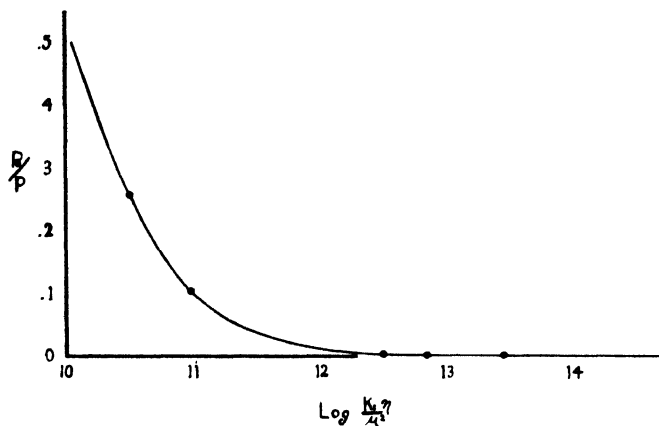


FIG. 1. Diagram showing the relationship between P_e/P and $\log \frac{K_e \eta}{(q.d.)^2}$. The points are calculated from the data on the system ethyl acetate-cellulose, and the smooth curve is that of figure 2 displaced along the horizontal axis an amount equal to $-\log r^2/8$.

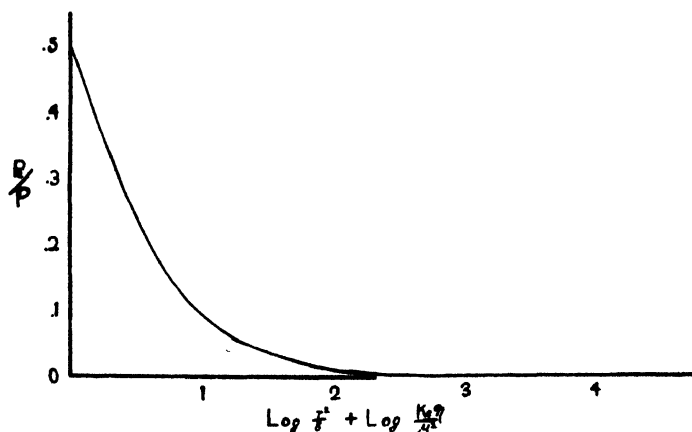


FIG. 2. Theoretical curve plotted from equation 5 showing the relationship between P_e/P and $\log \frac{r^2}{8} + \log \frac{K_e \eta}{(q.d.)^2}$.

figure 1 is taken to be a measure of $\log r^2/8$, a term found in the equation for the curve of figure 2 but not in that of figure 1. $\log r^2/8$ then becomes -10.030 . r is equal to 2.74×10^{-5} cm. = 0.274 micron.

The evaluation of r and $(q.d.)'$, the true electric moment, may be arrived at somewhat more directly by the following method:⁴ According to the considerations of Bull, $P = P_s + P_e$. By combining this equation with equations 3 and 4 and using the ideal value of the electric moment, $(q.d.)'$, one obtains the relationship:

$$P = \frac{\eta HK_s}{(q.d.)'} + \frac{8(q.d.)' H}{r^2}$$

$$(q.d.)' = \frac{\eta HK_s}{P} + \frac{8(q.d.)'^2 H}{Pr^2}$$

But

$$q.d. = \frac{\eta HK_s}{P}$$

$$(q.d.)' = q.d. + \frac{8(q.d.)'^2 H}{r^2 P} \quad (6)$$

If $q.d.$ is plotted against H/P , a straight line of intercept $(q.d.)'$ and of slope $-8(q.d.)'^2/r^2$ will be obtained. Expressed in practical units (H in millivolts, P in cm. of mercury),

$$10^6 q.d. = 10^6 (q.d.)' - 2.01 \times 10^{-3} (q.d.)'^2 / r^2 \times H/P$$

We find that, evaluated by this method, r is 0.277 micron and $(q.d.)'$ has a value of 5.72×10^{-6} .

In these considerations r cannot be taken to mean more than the effective mean radius of the pores in the diaphragm, if we regard the diaphragm as being a bundle of capillary tubes. Moyer and Bull (26) calculated r for a cellulose diaphragm filled with a dilute sodium chloride solution, using an entirely different method. They obtained a value for r of 0.86 micron. Their value is subject to the same limitations as is this one. It is at least a remarkable coincidence that they are of the same order of magnitude.

This method of approach is the first attempt of which the writers are cognizant to verify quantitatively by means of streaming potential the electroosmotic back pressure effect postulated by Abramson and by Bull. The fact that the data on these ester-cellulose systems may be treated successfully by the method of Bull is significant, not only because it constitutes evidence in favor of the electroosmotic back pressure effect as a reality, but also because it constitutes a new justification of the applicability of Helmholtz's theory to electrokinetic studies involving purified organic liquids. The considerations of Bull and of Abramson are straightforward deductions from the Helmholtz theory as applied to streaming

⁴ This solution is an adaptation of one proposed to the authors by Professor F. H. MacDougall, to whom the authors are very grateful.

potential and to electroösmosis. They involve no assumptions not inherent in that theory. Therefore, if the Helmholtz theory is applicable to systems such as those under our consideration, the electroösmotic back pressure effect must exhibit itself in systems with conductivities as low as those encountered and with mean pore radii of the order of magnitude of that determined for a somewhat similar system by Moyer and Bull. The fact that the observations fit the theory in this case shows that a second essential requirement of the theory of Helmholtz is fulfilled by organic liquid-solid systems.

If the value for pore size just calculated is at all near the actual value in the diaphragm, it is entirely possible that these pores are below the critical range for the validity of the assumption that the double layer consists of two parallel plates, made in the derivation of the equation used in the calculation of $q.d.$ Considerations of this subject must await more definite knowledge concerning the nature of the double layer at organic liquid-solid interfaces.

SUMMARY AND CONCLUSIONS

The electroösmotic counter pressure theory has been investigated qualitatively and quantitatively. The results of this study can be rationalized with a high degree of success in terms of the counter pressure theory. This constitutes a second justification for applying the theory of Helmholtz to streaming potential studies involving organic liquids. The original justification is the fact that streaming potentials of such systems have been shown to be directly proportional to the pressures of streaming, as the Helmholtz equation demands. The effective mean pore size of a cellulose diaphragm containing ethyl acetate has been calculated in accordance with the back pressure theory and found to have the value of 0.27 micron.

REFERENCES

- (1) ABRAMSON, H. A.: J. Am. Chem. Soc. **50**, 391 (1928).
- (2) ABRAMSON, H. A.: J. Gen. Physiol. **15**, 279 (1932).
- (3) ABRAMSON, H. A., AND GROSSMAN, E. B.: J. Gen. Physiol. **14**, 563 (1931).
- (4) BIKERMAN, J. J.: Z. physik. Chem. **A163**, 378 (1933).
- (5) BRIGGS, D. R.: J. Phys. Chem. **32**, 641 (1928).
- (6) BRIGGS, D. R.: J. Am. Chem. Soc. **50**, 2358 (1928).
- (7) BRIGGS, D. R.: Cold Spring Harbor Symposia Quant. Biol. **1**, 14 (1933).
- (8) BULL, H. B.: Kolloid-Z. **60**, 130 (1932).
- (9) BULL, H. B.: Kolloid-Z. **66**, 20 (1934).
- (10) BULL, H. B.: J. Phys. Chem. **39**, 577 (1935).
- (11) BULL, H. B., AND GORTNER, R. A.: J. Phys. Chem. **35**, 456 (1931).
- (12) BULL, H. B., AND GORTNER, R. A.: Physics **2**, 21 (1932).
- (13) BULL, H. B., AND MOYER, L. S.: J. Phys. Chem. **40**, 9 (1936).
- (14) DUBOIS, R., AND ROBERTS, A. H.: J. Phys. Chem. **40**, 543 (1936).
- (15) ETTISCH, G., AND ZWANZIG, A.: Z. physik. Chem. **A147**, 151 (1930).
- (16) ETTISCH, G., AND ZWANZIG, A.: Z. physik. Chem. **A160**, 385 (1932).

- (17) GUOY, M. D.: J. phys. radium [4] **9**, 457 (1910).
- (18) HELMHOLTZ, H.: Wied. Ann. **7**, 337 (1879).
- (19) JENSEN, O. G., AND GORTNER, R. A.: J. Phys. Chem. **36**, 3138 (1932).
- (20) KOMAGATA, S.: Researches Electrotech. Lab. (Tokyo), No. 362 (1934).
- (21) LAUFFER, M. A., AND GORTNER, R. A.: J. Phys. Chem. **42**, 641 (1938).
- (22) MARTIN, W. M., AND GORTNER, R. A.: J. Phys. Chem. **34**, 1509 (1930).
- (23) MONAGHAN, B., WHITE, H. L., AND URBAN, F.: J. Phys. Chem. **39**, 585 (1935).
- (24) MOYER, L. S.: J. Gen. Physiol. **42**, 391 (1938).
- (25) MOYER, L. S., AND ABRAMSON, H. A.: J. Gen. Physiol. **19**, 727 (1936).
- (26) MOYER, L. S., AND BULL, H. B.: J. Gen. Physiol. **19**, 239 (1935).
- (27) REICHARDT, H.: Z. physik. Chem. **A166**, 433 (1933).
- (28) WHITE, H. L., URBAN, F., AND KRICK, E. T.: J. Phys. Chem. **36**, 120 (1932).
- (29) WHITE, H. L., MONAGHAN, B., AND URBAN, F.: J. Phys. Chem. **40**, 207 (1936).

THE KINETICS OF THE DESTRUCTION OF TYROSINE COMBINED IN THE EGG ALBUMIN MOLECULE BY ULTRAVIOLET RADIANT ENERGY¹

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The exposure of protein solutions to ultraviolet radiant energy results in the destruction of the protein-combined tyrosine, (6). The first-order destruction of tyrosine in solution by ultraviolet irradiation is indicated by the results reported previously by Arnow (1). Irradiation of phenylalanine results in the formation of a substance giving the Millon reaction, which is probably tyrosine (unpublished data). The present investigation deals with the kinetics of the destruction of protein-combined tyrosine during ultraviolet irradiation.

METHODS

Egg albumin was crystallized by the method of Cole (4) and recrystallized twice. Ammonium sulfate was removed by simple dialysis, followed by electrodialysis (3). The tyrosine content of irradiated egg albumin hydrolysates was determined colorimetrically by the Millon reaction (Folin and Marenzi (5)) or by a micro method previously reported (2). Twenty-two control determinations of the tyrosine content of non-irradiated crystalline egg albumin showed a mean value of 3.85 per cent (S. D. 0.05 per cent).

Approximately 8 per cent egg albumin solution, stored in an ice chest at 5–7°C. and preserved with a toluene-paraffin oil layer, was removed by means of a bottom side arm on the storage flask to prevent contamination by the surface layer of the preservative. An accurately measured volume (about 10 cc.) was diluted to 100 cc. with distilled water and a definite volume of dilute hydrochloric acid or sodium hydroxide solution in order to obtain the desired pH value.

Fresh solutions were prepared from the concentrated stock solution at

¹ The data in this paper were taken from a thesis submitted by F. W. Bernhart to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1938.

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he start of each irradiation, and the excess solution was discarded. Before each series of irradiations the pH of the solution was determined by means of the glass electrode, and the egg albumin concentration was estimated by nitrogen analyses.

A Burdick air-cooled quartz mercury arc was used as a source of ultra-violet radiant energy. This instrument was operated with a voltage drop of 70 volts across the arc. All solutions were irradiated at a distance of 19.5 cm. from the light source. Two different quartz mercury arcs were used during the experimental work.

Quartz test tubes (20 x 130 mm.) of approximately 25-cc. capacity, containing 18 cc. of egg albumin solution, were stoppered with rubber stoppers fitted with bent glass tubes which allowed free entrance of air. In the irradiations which were carried out under nitrogen, the dissolved oxygen was displaced by alternate evacuation and bubbling of nitrogen through the egg albumin solution (to which 0.02 cc. of *n*-heptyl alcohol had been added to inhibit foaming) contained in the quartz irradiation tube. After this process had been repeated five times, the tube was sealed. The irradiations were carried out in a constant-temperature water bath at 25°C. \pm 1°.

KINETICS OF COMBINED TYROSINE DESTRUCTION

The results of the tyrosine analyses are given in table 1. T represents the millimoles of combined tyrosine present in 1 liter of egg albumin solution.

Analysis of the data indicates that the destruction of protein-combined tyrosine in these experiments does not occur as a zero-order, first-order, or second-order process. Inspection of the data indicates the possibility that two opposing reactions are occurring in the irradiated solution. After an initial rapid change of tyrosine during the first few hours of irradiation, the rate of destruction decreases rapidly. This is not due to any known physical factor, such as precipitation of the protein.

The possibility exists that phenylalanine or other substances present in egg albumin may form, during the irradiation, tyrosine or a phenol that would give the Millon reaction. The following assumptions were made to test this possibility: (1) Tyrosine destruction is a first-order process. (2) Tyrosine, or a phenol, is formed during irradiation by a zero-order process.

If the above assumptions are made, the rate of change of combined tyrosine in irradiated egg albumin solutions is given by the expression

$$\frac{-dT}{dt} = k_1 T - k_2$$

where T is the tyrosine concentration at time t , k_1 is the first-order velocity constant of tyrosine destruction, and k_2 is the zero-order velocity constant of tyrosine or phenol formation.

TABLE 1
Tyrosine present in egg albumin solutions after irradiation

DESCRIPTION	ATMOSPHERE	<i>t</i>	<i>T</i> ₀ (EXPERIMENTAL)	<i>T</i> ₀ (CALCULATED)
		hours	millimoles per liter	millimoles per liter
Ultraviolet arc 2S; egg albumin concentration, 7.6 mg. per cubic centimeter; initial pH, 6.40; $k_1 = 0.030$; $k_2 = 0.024$	Air	0	1.63	1.50
		5	1.37	1.38
		7.5	1.36	1.34
		10.0	1.32	1.30
		12.5	1.31	1.26
		15.0	1.28	1.23
		20.0	1.17	1.17
		25.0	1.10	1.12
		35.0	1.00	1.03
		41.0	0.98	1.00
		68.0	0.89	0.89
Ultraviolet arc 2S; egg albumin concentration, 7.3 mg. per cubic centimeter; initial pH, 6.30; $k_1 = 0.030$; $k_2 = 0.020$	Air	0	1.55	1.49
		2	1.44	1.44
		4.1	1.38	1.39
		6.5	1.34	1.34
		11.0	1.28	1.26
		16.2	1.15	1.17
		22.5	1.12	1.09
		30.0	1.01	1.00
		41.0	0.94	0.91
Ultraviolet arc 1W; egg albumin concentration, 8.1 mg. per cubic centimeter; initial pH, 3.94; $k_1 = 0.01$; $k_2 = 0.0081$	Air	0	1.73	1.64
		6	1.59	1.59
		12	1.50	1.55
		24	1.47	1.45
		36	1.41	1.39
		48	1.30	1.32
		72	1.19	1.21
		96	1.10	1.13
		240	0.88	0.88
Ultraviolet arc 1W; egg albumin concentration, 8.1 mg. per cubic centimeter; initial pH, 9.03; $k_1 = 0.010$; $k_2 = 0.0075$	Air	0	1.72	1.64
		6	1.59	1.59
		12	1.51	1.54
		24	1.38	1.44
		36	1.33	1.38
		48	1.31	1.30
		72	1.18	1.19
		96	1.10	1.09
		144	0.96	0.97
		240	0.85	0.84

TABLE 1—*Concluded*

DESCRIPTION	ATMOSPHERE	<i>t</i>	<i>T</i> ₀ (EXPERIMENTAL)	<i>T</i> ₀ (CALCULATED)
		hours	millimoles per liter	millimoles per liter
Ultraviolet arc 2S; egg albumin concentration, 7.6 mg. per cubic centimeter; initial pH, 6.40; <i>k</i> ₁ = 0.017; <i>k</i> ₂ = 0.0168	Nitrogen	0	1.63	1.63
		10	1.52	1.52
		20	1.40	1.43
		29	1.33	1.38
		40	1.34	1.32
		52	1.25	1.25
		80	1.16	1.16
		100	1.10	1.11
		140	1.05	1.05
		190	0.95	1.01

Integrating this expression,

$$T = T_0 e^{-k_1 t} + \frac{k_2}{k_1} (1 - e^{-k_1 t})$$

The unknowns in this equation are *k*₁ and *k*₂. After solving for the constants from data in the various series of irradiations, theoretical values were calculated. Calculated and analytical values for tyrosine are compared in table 1. The underlined calculated value in each series of data is the value of *T*₀ used in calculating the other points.

The calculated and experimental values agree satisfactorily, except that tyrosine destruction is more rapid during the time interval between the beginning of irradiation and the first determination than is predicted by the equation. This initial rapid destruction is not observed in the irradiation experiment performed in an atmosphere of nitrogen. The explanation may be that the dissolved oxygen in the solution is present in a greater amount at the beginning of the irradiation than after a few hours of irradiation, when oxygen diffuses in from the air. Two irradiations at pH 6.40 showed that oxygen promotes tyrosine destruction. Identical egg albumin solutions were irradiated by the same light source, one solution being in contact with air, the other under nitrogen. The rate of tyrosine destruction, as shown by the first-order velocity constants, was approximately twice as great in the irradiated solution in contact with air.

REFERENCES

- (1) ARNOW, L. E.: J. Phys. Chem. **42**, 415 (1938).
- (2) BERNHART, F. W.: Proc. Am. Soc. Biol. Chemists **XXXII**, x (1938).
- (3) BERNHART, F. W., ARNOW, L. E., AND BRATTON, A. C.: Ind. Eng. Chem., Anal. Ed. **9**, 387 (1937).
- (4) COLE, A. G.: Proc. Soc. Exptl. Biol. Med. **30**, 1162 (1933).
- (5) FOLIN, O., AND MARENZEL, A. D.: J. Biol. Chem. **83**, 89 (1929).
- (6) LIEBEN, F.: Biochem. Z. **187**, 307 (1927).

ADSORPTION OF ACIDS BY SYNTHETIC RESINS

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In a previous paper (2) the adsorption of alkalis by phenol-formaldehyde resins was shown to be predominantly chemical in character, the adsorption maxima approximating those calculated on the assumption that no linkage through the phenolic hydroxyl groups occurred on polymerization. In the present investigation corresponding aromatic amine-formaldehyde resins were prepared, and certain striking differences between their adsorptive properties and those of the phenolic resins were noted.

PROCEDURE

A. Preparation of resins

The method of preparation of the resins was found to have a decided influence on their properties. The amine was dissolved in dilute hydrochloric acid, the required quantity of formalin (40 per cent) was added, and the solution was allowed to stand until gelation occurred. The gel was broken up, and purification from acid was effected either before or after drying. In the former case the red gel was stirred into approximately normal ammonium hydroxide, whereupon the color changed immediately to yellow, and then the mixture was allowed to stand overnight. The mixture was filtered, washed with cold water, with hot water until free from ammonium hydroxide, then with alcohol and ether, and dried. In the latter case the gel was dried at 100°C. or some other suitable temperature and purified as before. The purified gel was ground, screened, and graded to pass through 35 on to 100 mesh.

Some resins were prepared by using an equimolecular mixture of aniline and acetanilide, sufficient alcohol to dissolve the latter being used. After standing for 2 days at room temperature, the cherry-red liquor was poured into ammonium hydroxide and heated on a steam bath. Subsequent treatment was as before.

B. Adsorption measurements

About 0.2 g. of resin was weighed out into a bottle and a known volume of standard acid was added. After agitation for a measured time on a

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rotary shaker at room temperature ($25^{\circ}\text{C.} \pm 2^{\circ}$), the solution was filtered and analyzed. A number of resins were recovered by treatment with alkali and the adsorption redetermined. Blanks were run using both distilled water and standard alkali instead of acid, in order to test for acid not removed by washing.

RESULTS

Unlike the case of the phenolic resins, adsorption by the amine-formaldehyde resins is usually rapid, equilibrium being frequently attained within 24 hr. In figure 1 are shown results for typical aniline and *m*-phenylenediamine-

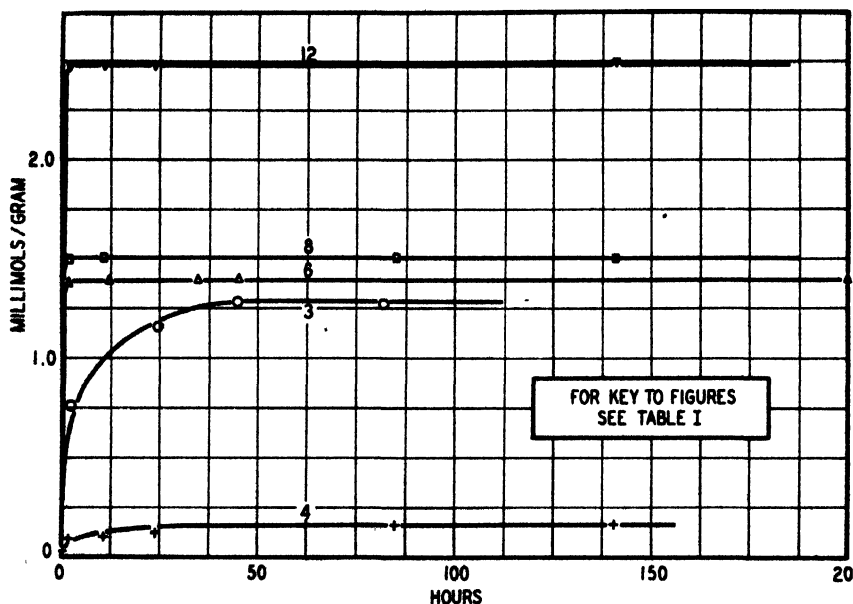


Fig. 1. Adsorption of 0.0198 *N* sulfuric acid by aniline and *m*-phenylenediamine resins

diamine resins with 0.0198 *N* sulfuric acid. No tests lasting longer than 400 hr. were made.

Equilibrium values for adsorption by the amine-formaldehyde resins are considerably smaller than those shown by the phenolic resins and are found to be sensitive to the proportions of reactants, temperature, etc. Table 1 gives the equilibrium adsorption for a number of resins from 0.0198 *N* sulfuric acid together with details of their preparation. Resin No. 5 was prepared from an equimolecular mixture of aniline and acetanilide.

Table 2 shows adsorption by several resins from 0.0198 *N* hydrochloric and sulfuric acids, the last two columns of the table showing adsorption by recovered and heated resins, respectively.

INTERPRETATION AND DISCUSSION OF RESULTS

As for the phenolic resins, adsorption appears to be chemical in character; indeed, the rate of adsorption by the amine-formaldehyde resins is much greater than for phenolic resins. Most outstanding, however, are

TABLE 1
Adsorption of acid and conditions of preparation of resins

NO.	MOLAR RATIO HCl AMINE	MOLAR RATIO HCHO AMINE	INITIAL MIXING TEMPERATURE	TEMPERATURE OF DRYING	EQUILIBRIUM ADSORPTION
Aniline resins					
			°C.	°C.	millimoles per gram
1	1.1	2.4	25	100	0.32
2	1.2	2.2	100	100	0.08
3	0.7	2.6	25	25	1.28
4*	1.2	2.1	25	100	0.15
5	1.2	2.1	25	100	0.75
<i>m</i> -Phenylenediamine resins					
6	2.4	4.0	25	100	1.40
7	2.2	4.0	25	100	1.55
8*	2.2	4.0	25	100	1.50
9	2.2	4.0	0	25	1.48
10*	2.2	4.0	0	25	1.50
11	2.2	4.0	100	100	1.55
12*	2.2	1.2	25	100	2.47
13*	2.2	1.2	25	25	2.75

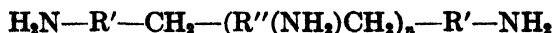
* Dried before treatment with ammonia.

TABLE 2
Equilibrium adsorption of hydrochloric and sulfuric acids

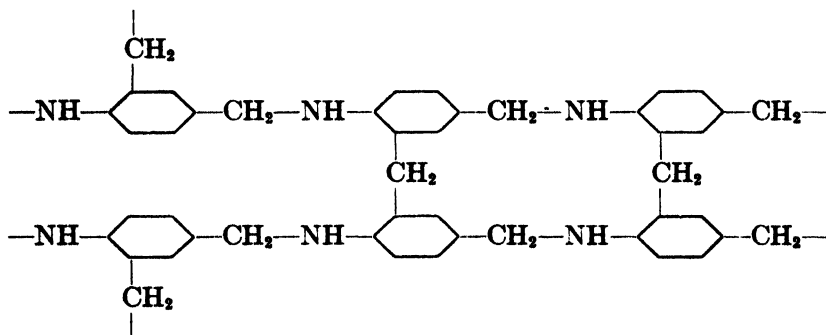
NO.	HYDROCHLORIC ACID	SULFURIC ACID	SULFURIC ACID BY RECOVERED RESIN	SULFURIC ACID AFTER HEATING AT 100°C. FOR 72 HR.
	millimoles per gram	millimoles per gram	millimoles per gram	millimoles per gram
1	0.40	0.32		
2	0.13	0.08		
7		1.50	1.55	
10		1.50	1.56	1.21
11	1.50	1.55		
13		2.75		1.64

the small values for equilibrium adsorption of the amine resins, if they are saturated at this acid concentration, i.e., if the equilibrium acid adsorption has become independent of acid concentration as was the case for

alkali and the phenolic resins (2). If polymerization occurred without affecting the characteristic substituent group, as is apparently the case with the phenols and formaldehyde, compounds of the type



should be formed. The aniline resin of this type might be expected to have an equilibrium adsorption maximum of about 9.0 millimoles per gram, the *m*-phenylenediamine resin of 15.8 millimoles per gram.² None of the resins prepared gave values exceeding one-fifth of these maxima. It is clear that, unless the majority of the amino groups in some way are rendered structurally inaccessible to acid in the interior of the mass, they must be involved in the reaction between amine and formaldehyde. The latter view seems the more probable, as there is considerable chemical evidence (3, 4) that in the presence of sufficient acid and excess formaldehyde condensation occurs at the amino groups as well as in the nucleus. Thus, with aniline a compound similar to



may be obtained. Undoubtedly condensation would not be complete at all amino groups, thus accounting for the variations in the equilibrium adsorption of table 1 with reaction conditions. Low temperatures of drying and low formaldehyde-amine ratios, as might be anticipated, appear to discourage condensation through the amino group, thus leading to resins of greater adsorptive power. The initial mixing temperature seems to be of little importance, possibly because of the extreme rapidity of the reaction. Heating the dry resin usually causes a darkening in color and a decrease in adsorptive power, indicating a further polymerization. In contradistinction to the results of Adams and Holmes (1), drying with acid still present appears to have little effect upon the adsorptive power, as shown by comparison of resins 7 and 8 and 10 and 11 of table 1.

An attempt was made to prepare aniline resins of greater adsorptive power by protecting the amino group during resinification. Formalde-

² Calculated on the formulas $\text{C}_6\text{H}_2(\text{NH}_2)(\text{CH}_2)_{1/2}$ and $\text{C}_6\text{H}(\text{NH}_2)_2(\text{CH}_2)_{1/2}$, respectively. See reference 2.

hyde and acetanilide alone, however, reacted only slowly and could not be made to give a satisfactory resin. Use of an equimolar mixture of acetanilide and aniline gave a resin of somewhat higher adsorptive power (No. 5). This was still inferior to the best aniline resin.

SUMMARY

The rates of adsorption of sulfuric and hydrochloric acids by aniline and *m*-phenylenediamine resins have been determined. Unexpectedly low values for the equilibrium adsorption were obtained, indicating that condensation probably occurs through the amino groups as well as through the nucleus.

REFERENCES

- (1) ADAMS, B. A., AND HOLMES, E. L.: J. Soc. Chem. Ind. **54**, 1T (1935).
- (2) AKEROYD, E. I., AND BROUGHTON, G.: J. Phys. Chem. **42**, 343 (1938).
- (3) ELLIS, C.: The Chemistry of Synthetic Resins, Vol. I. Reinhold Publishing Corporation, New York (1935).
- (4) FREY, K.: Kunststoffe **25**, 305 (1935).

CATAPHORESIS IN INSULATING MEDIA¹

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INTRODUCTION

The phenomenon of cataphoresis in aqueous media has been studied in great detail by colloid chemists during the last few decades. Cataphoresis in organic hydrophilic media has been the subject of a comparatively few papers only, and cataphoresis in *insulating* liquids is a problem which, although described sometimes in a more qualitative sort of way (7, 8), has not up to now been the subject of a quantitative experimental investigation, as far as the author knows. However, it seems desirable that this field be opened for research, not only from the standpoint of physical chemistry, but also from the standpoint of technical applications, since electrophoretic processes in liquid insulators play a certain, partly important rôle (5).

The author has thought of starting a series of investigations on these lines, the results of the first of which are described in the following paper. First a theoretical part will be presented, dealing with some aspects of cataphoresis in insulating media. The experimental part will describe the results that have been obtained on polystyrene suspensions in insulating media, chiefly mineral oil. The preparation of the necessary suspensions, the microscopic method of measuring cataphoretic mobilities, and the question of influencing the electrical charge by adding suitable electrolytes to the system will be dealt with.

I. THEORETICAL

1. THE BASIC EQUATION OF CATAPHORESIS

The basic equation of cataphoresis (4), first deduced by Helmholtz and later more generally by Smoluchowski, is:

$$u = \frac{\epsilon \zeta E}{4\pi\eta} \quad (1)$$

¹ This paper is an abridged presentation of a report submitted to the British Electrical and Allied Industries Research Association, London, England.

where u = the velocity of the particles, ϵ = the dielectric constant of the medium, ζ = the electric potential between the bulk of the dispersing phase and the phase boundary, E = the applied electric field, and η = the viscosity of the medium. The validity of the factor 4 has recently become somewhat doubtful, but it is not necessary to consider this point (2).

It should be pointed out that the deduction of equation 1 is valid only as long as the conductivity of the medium is at least one or two orders greater than that of the particle. One can easily show what will happen if this condition is not fulfilled. In figure 1a the electric field around a spherical particle is shown, if the above condition holds. Now suppose the electric conductivities of the phases to be equal; then no refraction of the field lines occurs, and they will pass straight across the particles, as shown in figure 1b. In consequence the tangential component of the field, which alone is

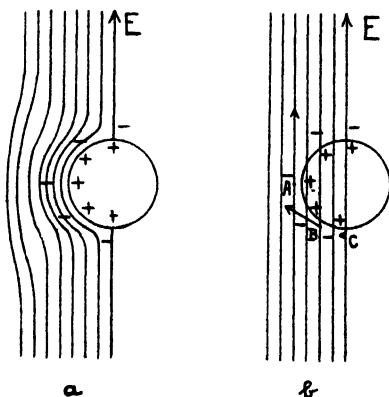


FIG. 1. Schematic diagram concerning validity of Helmholtz equation for insulating media

acting in shifting the medium, will have its full value only at points like A; in B it has only a fractional value of the total, and in C it is zero. This circumstance will reduce u , especially if the conductivity of the sphere surpasses that of the medium.

The condition attached to equation 1 is easily fulfilled with aqueous media, but not generally with insulating ones. It is certain, for instance, that equation 1 does not hold for the cataphoresis of water drops in oil. However, we may expect its validity in our special system with a reasonable degree of accuracy. The conductivity of oil at room temperature and possessing the usual humidity is of the order of 10^{-13} to 10^{-14} reciprocal ohms per centimeter, whereas that of the artificial resins is certainly not higher than 10^{-15} to 10^{-16} reciprocal ohms per centimeter, that is, it is at least one or two orders of magnitude lower.

Also it should be mentioned that equation 1 is valid for particles of any

shape, not spheres only, in case the above-mentioned condition holds. This is of special interest for us, since the particles, as may be seen under the microscope, are by no means always spherical, but sometimes pronounced bacilli (see part II, section 3). Still equation 1 remains applicable.

Let us now consider the special aspects arising in applying equation 1 to organic insulating media. In discussing the various factors in equation 1, ζ , the electrokinetic potential, is certainly the most important. Accordingly it should be dealt with more in detail in the following sections. Here we merely assume that for a given system of components it has a definite value, and we shall see the way in which the other three factors, namely, E , ϵ , and η in organic liquids, affect the cataphoretic velocity.

A. Field strength

Owing to the low conductivity of oils no polarization phenomena at the electrodes will occur. Gas liberation at the electrodes is in fact one of the difficulties in electrophoretic measurements in aqueous solutions. In insulating media no such processes occur; this is a definite advantage.

For similar reasons the field strength may be given much higher values than in aqueous suspensions, without requiring any appreciable power from the generator, and without the slightest risk of overheating the system. Thus by increasing E within certain limits (see part II, section 3) we can increase u as well, both being proportional.

B. Dielectric constant

In aqueous media ϵ is 81. There is an uncertainty as to its value in the double layer, owing to the high ionic content of the latter. Ions tend to affect the value of ϵ , generally increasing it. This difficulty again does not exist in insulating liquids, owing to their very low ionic content.

On the other hand, the value of ϵ is much lower than in water, and this circumstance reduces the mobility of the particles considerably. With an average value of 2.3 for ϵ in insulating media, the mobility will be reduced about thirty-five times as compared with water.

C. Viscosity

Finally the value of η must be considered. Whereas in water it is 0.01 poise, in organic solvents containing oil it becomes higher. Mineral oil has a viscosity at room temperature of about 0.2 to 0.5, but that of other organic solvents is much lower, the viscosity of xylene, for instance, being 0.0065. Since our system consists of a mixture of oil with other solvents, medium viscosities will result, of the order of 0.05, as measured by the oscillation-viscometer (see part II, section 3). This circumstance again reduces the mobility by a factor of about 5.

2. STRUCTURE OF THE DOUBLE LAYER

The different factors in equation 1 having been surveyed briefly, the principal one remains, namely, ζ . This will be decisive for the possibilities of cataphoresis in insulating liquids. There are two different approaches with regard to ζ , namely, its geometrical structure, so to speak, and its physical causes. Both are important from our point of view. We shall first discuss the structure of the double layer, without entering into the possible sources of the potential difference.

The theory of the diffuse double layer² cannot be given here in detail, but some of the resulting equations will be quoted. We introduce the notation:

$$a = \frac{8\pi F c_0}{\epsilon} \quad (2)$$

where F = the Faraday constant and c_0 = the concentration of (monovalent) ions in the liquid phase; further

$$\alpha = \frac{F}{RT} \quad (3)$$

where R = the gas constant and T = the absolute temperature; and

$$\beta = \sqrt{a\alpha} \quad (4)$$

The total potential difference between the boundary and the bulk of liquid phase should be φ_0 (which is not identical with ζ , see part I, section 3), and the surface charge density at the boundary should be ω . The theory then gives a definite relation between φ_0 and ω . This relation can be given in finite form in two special cases.

First let us assume that

$$\varphi_0 < \frac{1}{\alpha} \quad (5)$$

then

$$\omega = \frac{\epsilon}{4\pi} \left(\frac{1}{r_0} + \beta \right) \varphi_0 \quad (6)$$

where r_0 = the radius of the (spherical) particle.

Second let us assume the radius of the particle to be large as compared with the radial dimension of the double layer; then

$$\omega = \frac{\epsilon}{2\pi} \sqrt{\frac{a}{\alpha}} \sinh \frac{\alpha\varphi_0}{2} \quad (7)$$

² See reference 4.

Equation 6 or 7 shows that the above theory allows one of the two quantities φ_0 and ω to be dealt with as a free variable; the other is then determined by the structure of the double layer. This indicates that in discussing the physical sources of the potential difference one must distinguish between those sources that primarily determine φ_0 and those that determine ω (see next section).

We now introduce another quantity, the so-called "equivalent thickness" of the double layer, δ : namely, that thickness which it would possess if the diffuse layer in the liquid were replaced by a surface layer.

Our first case (equation 6) yields:

$$\delta = \frac{1}{\beta} \quad (8)$$

whereas the second (equation 7) gives:

$$\delta = \frac{1}{\beta} \cdot \frac{\frac{\alpha\varphi_0}{2}}{\sinh \frac{\alpha\varphi_0}{2}} \quad (9)$$

As can be seen by equation 4, the equivalent thickness of the double layer is inversely proportional to the square root of the ionic concentration c_0 of the solution. Putting in numerical values, we have for *insulating* liquids (all data in absolute units):

$$\alpha = 1.2 \times 10^4$$

$$a = 3.2 \times 10^{12} c_0$$

and

$$\beta = 2 \times 10^8 \sqrt{c_0}$$

Taking for c_0 the likely order in oil of 10^{-11} moles per liter (9) (not the total concentration of electrolyte, which is much larger, but that of free ions), we have from equation 8:

$$\delta = 1.7 \times 10^{-3} \text{ cm.}$$

This will be the correct order as long as the first case holds, that is, for

$$\varphi_0 < 25 \text{ millivolts}$$

For larger potentials, on the other hand, the second approximation could be used. Take $\varphi_0 = 200$ millivolts; δ is then, from equation 9,

$$\delta = 6 \times 10^{-5} \text{ cm.}$$

whereas the order of magnitude of the particle radius (see part II, section 3) is 10^{-3} to 10^{-4} cm. The approximation, therefore, would be just appli-

cable. Which of the two possibilities actually holds for our system depends on the magnitude of φ_0 and will be seen from section 3 of part II. In any case the equivalent thickness is between 10^{-3} and 10^{-5} cm., a point to which reference will be made in the following section.

3. ORIGIN OF BOUNDARY POTENTIAL

We come to the last point of our theoretical considerations, namely, the question as to the *origin* of the potential. There are generally two possibilities; the first is a thermodynamic cause, the other is a surface effect.

A. Thermodynamic potential

In a system of two phases any component is, according to thermodynamics, distributed in both phases in finite amounts, even if the concentrations are sometimes negligibly small. Thus in our system there is a certain amount of oil dissolved in the resin phase, and *vice versa*.

As long as the components are electrically neutral, this distribution has naturally no effect upon the electric potential, but becomes effective if they are ions. Again the theory will not be given, only the final equation, namely,

$$\varphi_0 = \frac{1}{\alpha} \log \sqrt{\frac{\gamma_k}{\gamma_a}} \quad (10)$$

where γ_k and γ_a are the distribution coefficients between the two phases for cation and anion of a dissolved (monovalent) electrolyte. If, therefore,

$$\gamma_k \neq \gamma_a$$

then

$$\varphi_0 \neq 0$$

Actual measurements between organic solvents and water have revealed the existence of thermodynamic potentials of the order of 0.5 volt. Since the oil always contains electrolytes (organic acids, water, etc.), such potentials might easily arise in our system.

Another possibility on a thermodynamical basis is given, if one of the phases behaves as a reversible electrode for a certain ion. Such is the case with glass, which is a reversible electrode for the hydrogen ion. Since artificial resins are often of vitreous structure, some might act as reversible electrodes too.

Since, in our special case both phases are organic, γ_k and γ_a are not likely to differ from unity by several orders of magnitude. This circumstance would indicate a smaller potential, and thus a smaller mobility than with aqueous media.

Another circumstance, on the other hand, points to an increase of the potential, as compared with aqueous solutions. It should be recalled here that φ_0 and ζ are not identical. φ_0 is the total difference between the bulk of the two phases. Considering ζ , on the other hand, it is certain that a liquid layer of width d , of molecular order of magnitude, will adhere strictly to the solid phase. According to the deduction of equation 1, ζ must be reckoned only from the point which just begins shifting, and ζ , accordingly, will be smaller than φ_0 . This is proved experimentally for aqueous and other hydrophilic media, ζ being of the order of 50 millivolts. It is obvious that the divergence between φ_0 and ζ is the more pronounced, the smaller the equivalent thickness of the double layer, δ , as compared with d .

It has been shown in section 2 that δ in our system will vary from 10^{-3} to 10^{-5} cm., whereas in aqueous solutions it is 10^{-6} to 10^{-7} cm. If d is assumed to be of the order of 10^{-7} cm., it can be seen that, whereas for water ζ is only a fraction of φ_0 , in oil they will be almost identical. In spite of the fact that φ_0 is probably smaller for oil than for water, ζ , in insulating liquids, will still be appreciable.

B. Adsorption potentials

The potential is not always due to thermodynamic causes, but is frequently originated by ionic adsorption on the surface. In these cases ω is the fundamental quantity, the potential simply following from it according to equation 6 or 7.

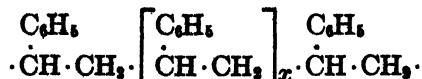
An adsorption potential might be due to physical or chemical forces. *Physical* adsorption is generally controlled by an adsorption isotherm, such as that of Freundlich or Langmuir. The total surface charge is then

$$\omega = F(n_k a_k - n_a a_a) \quad (11)$$

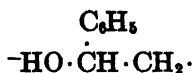
where n_k , n_a = the valences, and a_k , a_a = adsorbed moles per cm.² for cation and anion. It is difficult to state, without a more detailed investigation, whether or not this kind of potential plays a dominant rôle in our systems, but they certainly will influence any other potential, since surface forces of the kind considered are always present. *Chemical* adsorption usually occurs on surfaces of acidic or basic absorbents. The process is similar to the dissociation of weak acids or bases, the particles behaving like very large anions or cations. It is not impossible that such a charge is realized in our systems. Let us consider polystyrene, since the experiments have been carried out with this material. It is a polymerization product of styrene:



The final product may be represented thus:



This compound does not appear to be either acidic or basic. Still one has to remember that the phenyl group has an affinity for the hydroxyl group (or any other negative group), as is evident from compounds like phenol, nitrobenzene, and the like. Correspondingly, the free valence at the end of the chain might easily pick up a hydroxide ion, thus:



acquiring a negative charge by this means.

Such charges are well known from a number of adsorbents in aqueous solutions, and it is possible that polystyrene assumes a similar one.

The theory of electrolytic dissociation as applied to colloids allows the surface charge to be calculated under certain assumptions; when the surface charge ω , is known, the potential can be computed by means of equation 6 or equation 7.

It might be concluded from the last section that a positive result of cataphoresis experiments might be expected, either because of a thermodynamic potential at the boundary resin-oil, or because of ionic adsorption.

II. EXPERIMENTAL

1. PREPARATION OF THE SUSPENSION

Polystyrene, used in the following experiments, is easily soluble in insulating organic solvents, among which *m*-xylene has been specially chosen, owing to its high boiling point (139.4°C.) and consequently low inflammability.

A standard solution was prepared by dissolving 2.5 g. of polystyrene in 10 cc. of xylene. This solution was applied in the form of drops from the same pipet, each drop containing 0.0058 g. of the resin.

This solution of polystyrene is a typical colloidal solution. According to Staudinger (3) it is an eucolloid, possessing particles of a chain length greater than 2500 Å. For the purposes of cataphoresis, however, it did not seem to be suitable, probably because its particles are not sufficiently charged. Although no final conclusion can be drawn from this observation, it appears to be in contradiction to the possibility of a chemical adsorption. Since both of the other mechanisms, namely, phase potentials and physical adsorption, require a more pronounced two-phase structure, the method of procedure was clearly indicated. Instead of using a colloidal solution, a suspension had to be tried.

This can be obtained by the method of slow precipitation. Polymeric styrene is practically insoluble in mineral oil, and in replacing the xylene by oil, the resin can be precipitated. Performing this process very carefully, it is *possible* (not with any resin of course) to reduce the precipitation velocity considerably, obtaining in this way suspensions that are stable, for a certain time at least.

Three drops of standard solution were added to 10 cc. of xylene, and then carefully increasing amounts of mineral oil. A low-viscosity oil was used throughout this investigation. The solution remained clear after the first portions of oil were added, the first sign of turbidity appearing rather sharply. Further addition of oil increased the turbidity up to a certain limit, after which it remained constant.

Preliminary experiments revealed that cataphoresis tests are possible with such suspensions, thus fully justifying our conclusions with regard to the necessity of a second phase. The presence of two distinct phases could be proved by microscopic examination of the suspensions.

Suspensions or emulsions are frequently prepared with stabilizing agents, the rôle of which probably is to coat the particles with a thin layer which in its turn assumes a charge (gelatin and similar proteins).

To find a suitable stabilizer, a suspension was made as just described. Four small test tubes were filled with 1 cc. each. No. 1 had no added material whatever. To No. 2 one drop of liquid ethyl stearate, to No. 3 one drop of molten naphthalene, and to No. 4 one drop of a chlorinated diphenyl were added.

A comparison of the four tubes, after a few hours standing, showed a precipitate in each, the amount of which was decidedly least in No. 4, thus indicating that chlorinated diphenyl can be used as a stabilizer. Further experiments showed that it had to be present in a concentration of about 10 per cent in order to have a pronounced beneficial effect. It is possible that part of the effect is due to an increase of viscosity of the suspension.

2. THE MICROSCOPIC METHOD

Cataphoresis tests were carried out by two different methods: a more qualitative one, by producing visual deposits on metallic electrodes, and another, more quantitative, by microscopic investigation of the motion. Since the first method led to results that are important from the standpoint of possible practical applications, it will be dealt with elsewhere.⁸ Here only the microscopic method will be considered.

This method must take account of the complications arising from an electroösmotic effect near the walls. The resulting and observable motion of the particles is the sum of two components: first, of the real cataphoretic

⁸ A paper, "Electrodeposition of Synthetic Resins", is to appear in *Industrial and Engineering Chemistry*.

velocity, being equal at any depth of the trough that contains the liquid and the electrodes; second, of an electroosmotic shift of the liquid, which is the result of a surface charge at the boundary wall-liquid.

Smoluchowski developed a quantitative theory to overcome this difficulty. The assumptions are only (1) that the trough is a closed one and (2) that the walls have a higher specific electrical resistance than the liquid. This means that the electrical intensity has the same value in the whole trough. This latter condition is easily fulfilled with aqueous solutions. If, then, the actual velocity is measured in two definite heights, the theory allows the true cataphoretic velocity to be computed from these two data.

In our insulating system, however, the second condition is not fulfilled, since glass has about the same conductivity as oil, and the surface of glass, containing some adsorbed water, has an even higher conductivity. If a trough containing two parallel electrodes at a certain distance were filled with oil, most of the field lines would concentrate in the space between the electrodes and the glass, the middle portion of the trough possessing a low electrical field, the value of which would not be known exactly.

Now the best criterion for good working conditions is the reversibility of velocity when the voltage is being reversed. When, however, actual experiments with our suspension in a trough as just described were carried out, a velocity was observed, which, though changing its magnitude in reversing the voltage, did not change its sign. This is a clear indication that the real cataphoretic velocity is small, and is superimposed by insignificant mechanical currents not within the experimenter's control.

There are two ways out of this difficulty. One would be to use a trough of quartz, which has a higher specific resistance than oil, though even then it is doubtful whether the surface would not give rise to difficulties. The other method, actually used, was an arrangement in which disturbances from the neighboring walls were eliminated as far as possible. Whereas with a trough with parallel electrodes a uniform field is aimed at, in our device an inhomogeneous field was built up, dropping rapidly with increasing distance from the center of the trough, so that its value near the walls was already too low to lead to any serious complication. This arrangement is not ideal, but for highly insulating liquids is still suitable, as the experiments showed.

The trough is shown in figure 2. *a* is a glass microscope slide, *b* and *b'* are two strips of a slide cemented to *a* by means of shellac. *c* is one half of another slide glass, placed just at the top of *b* and *b'*. The depth of the trough was 1.25 mm. The electrodes, *d* and *e*, consisted of copper wires, about 1 mm. in diameter, bent to the shape shown in figure 2. If the separation of the central points of the wires is very small, then the field conditions just described will be fulfilled.

The voltage was provided by a d.c. potentiometer. The rotating sup-

port of the microscope must be made of insulating material, in order to avoid unwanted fields through leakage across the table. For the same reason it is better to use batteries instead of the mains.

The use of the trough is as follows: The bottom and top pieces are placed together upon the microscope, and the liquid is allowed to run by means of a pipet into the free space. Then the electrodes are placed carefully in the liquid. The microscope must be fitted with an ocular scale, which allows the separation to be read. It is easy to adjust the objective lens to a point at which the circular copper boundaries appear quite sharp. We then know that the plane of observation coincides with the center plane of the trough.

Measurements are made by observing by means of a stop-watch the time that any fixed particle requires to travel a given distance marked on the ocular scale. A number of readings must be taken, reversing the voltage after each of them.

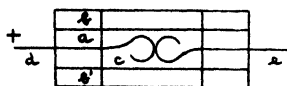


FIG. 2. Diagram of microscopic trough

3. MICROSCOPIC MEASUREMENTS

Equation 1 was used to compute ζ from the velocity measurements. The field strength E was calculated by assuming that the field at the *central point* itself is uniform, therefore given by V/D , if V is the voltage shown by the potentiometer, and D the separation. The latter was measured in divisions of the ocular scale, one division corresponding to 0.0061 cm. The velocity u was given by $0.0122/t$ in cm. per second, since the path travelled by the particles was two divisions (0.0122 cm.), and t was the time in seconds required for this distance.

The dielectric constant of the mixture was assumed to be 2.3, since this is the value for *m*-xylene and very nearly that for mineral oils. The percentage of chlorinated diphenyl might have increased the total value somewhat, but not considerably. Measurements of the dielectric constant have not been carried out.

As to the viscosity, its value could not be estimated with any degree of certainty, and accordingly measurements were taken. A new apparatus, the oscillation viscometer, has been used, as developed by R. V. Southwell and the author. The instrument is described in a British patent (6) and in a recent paper (1), hence only a few words will be included here in regard to its principle.

A diagram of part of the apparatus is given in figure 3. An alternating air pressure by means of a pump (not shown in the figure) is acting from a

upon the tube b containing the liquid in question (*c* is a temperature bath), and the tube d containing mercury. Oscillations will be set up, the amplitudes of which are inversely proportional to the resistances. That of the mercury tube is given by its gravity (below the resonance frequency); that of the oil tube by its viscosity. Hence the viscosity can be computed from the ratio of the amplitudes.

The amplitudes are read by means of two auxiliary tubes *e*, containing water or benzene, placed in front of a scale. The whole motion is quasi-stationary, so that a direct reading is possible, in contrast to other known viscometers.

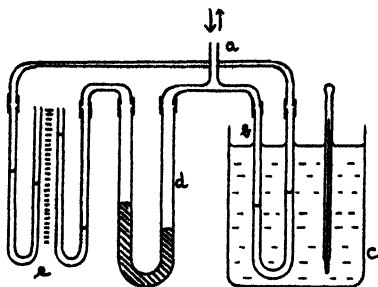


FIG. 3. Diagram of Gemant-Southwell oscillation viscometer

The theory will not be given, but only the final equation for computing the viscosity. It reads as follows:

$$\eta = \frac{\rho_m}{8r_m^3} \left(\frac{g}{\omega} - h_m \omega \right) \frac{r^4}{h} \cdot \frac{a_m}{a} \quad (12)$$

where ρ_m = the density of mercury, r_m = the radius of the mercury tube, g = the gravity constant, $\omega = 2\pi$ times the frequency of the alternating pressure, h_m = half the length of the mercury column, r = the radius of the oil tube, h = half the length of the oil column, a_m = the amplitude of the indicator connected with the mercury tube, and a = the amplitude of the indicator connected with the oil tube.

By means of this apparatus the viscosity of our system was found to vary somewhat around an average value of 0.05 poise.

Considering all data the following equation may be derived from equation 1:

$$\zeta = 18.2 \times 10^3 \frac{D}{tV} \quad (13)$$

in which D is measured in divisions of our ocular scale, t in seconds, V in volts, and ζ is obtained in millivolts.

The size of the particles could be estimated to about 10^{-6} to 10^{-4} cm.

One had the impression that the size increased with advancing age of the suspension.

The *shape* of the particles seemed to be spherical, in general, but in a number of cases, especially in suspensions older than one day, the particles appeared to be longish, like bacilli. In certain cases these "bacilli" exhibited a pronounced oscillatory motion of a Brownian type.

When the voltage was switched on, motion immediately started, and showed the correct change of sign when reversing. Also it was noticed that not all the particles showed the same speed. This might be due partly to the inhomogeneity of the field, but partly to a non-uniformity of charge. Humphry and Jane have observed the simultaneous occurrence of both charges in rubber sols. This does not appear to be the case in polystyrene dispersions, or, if so, to a very small extent.

According to equation 1 the velocity should be proportional to the field strength. This is certainly the case and can be tested experimentally, though strictly quantitatively only in a limited range. If the field is below a certain value, u is so small that it is being masked by other unavoidable weak currents of mechanical origin. If, on the other hand, E is too large, secondary effects, well known from high tension technics, are set up, especially dielectric attraction of components of higher dielectric constant in an inhomogeneous field. This latter effect, proportional to E^2 , can decidedly be observed in higher fields, since the resin has a dielectric constant about 2.5, that is, slightly higher than that of oil. Accordingly the law of proportionality can be tested only between this upper and lower limit.

A typical observation will be given: 10 cc. of solution was prepared according to the directions given in section 1 of part II, having a xylene-oil ratio of 1:2 and containing one drop of standard solution. A few hours after preparation the trough was filled, D being 3.55 and $V = 10$. Migration was anodic. The successive readings for t were as follows: 18, 18, 16, 18, 20, 14, 20, 15, 18, 15, with an average of 17. Applying equation 13 we obtain $\zeta = -38$ millivolts. The same solution contained much less particles the next day, with $\zeta = -34$ millivolts.

There seems to be no appreciable change of the charge with time. On the third day only very few particles could be detected, and no reliable readings were taken.

The potential has the same order of magnitude as in aqueous systems, with the actual values somewhat lower. This confirms our previous theoretical considerations. In section 3 of part I it has been shown that φ_0 is certainly smaller than in water. The same will hold if the potential is not thermodynamic but due to adsorption, since the ionic concentration of the liquid itself is extremely little. On the other hand, it was shown that

the electrokinetic potential ζ is probably a much higher fraction of the total than in water. Thus ζ is very likely of about the usual order.

If then $\varphi_0 = \zeta$ is assumed to hold, which is very likely, since $\delta \gg d$, then the order for φ_0 of 30 millivolts can be concluded. Thus the first approximation of section 2 of part I (equations 6 and 8) will hold fairly well, whereas the second is unlikely. In aqueous systems the opposite is the case: owing to larger values of φ_0 and the small values of δ the second approximation (equations 7 and 9) holds much better than the first. Reverting to the calculation at the end of section 2 in part I, δ , the equivalent thickness of the double layer, turns out to be of the order of 10^{-3} cm.

4. INFLUENCE OF ELECTROLYTES

In aqueous systems negative particles generally become stabilized by alkalis and precipitated by acids. We wanted to see whether a similar effect could be traced in insulating media. The results showed that there is such an effect, though not so marked as in aqueous media, and that it is apparently reversed. Acids seem to stabilize, alkalis to precipitate by reversing the sign of charge.

Owing to the low solubility of electrolytes in insulating systems, it was to be expected that the effect should not be pronounced. The question of why the reversal took place is not so easy to answer. It seems to indicate that the adsorption was not of a chemical nature, since in this case alkalis with their OH^- ions ought to increase the negative charge. This conclusion should not, however, be stated definitely, without having carried out further experiments on this point. Should the conclusion prove correct, then either physical adsorption or thermodynamical phase distribution must be considered, in agreement with the conclusion reached in section 1 of part II. The acids added were hydrochloric acid and picric acid; the alkali potassium hydroxide. Owing to the very poor solubility of these substances, small amounts of ethyl alcohol as "mediator" were added to some samples. In a preliminary experiment it was found that 3 per cent of alcohol does not by itself affect the ζ -potential appreciably, the latter being -34 millivolts.

Picric acid. 0.3 cc. of alcohol in which a few crystals of picric acid were dissolved were added to 10 cc. of the suspension. On the first day ζ was -13 millivolts, on the second day -18 millivolts, on the third -14 millivolts. The following should be remarked: (1) The particles had a pronounced bacillus-like shape. (2) The motion was extremely uniform. (3) The life of the suspension was decidedly longer than normally. On the third day very reliable readings could be taken, which was not the case with the original suspension. (4) ζ remained negative, but seemed altogether smaller than normally.

Another experiment was carried out with a suspension to which picric

acid was added directly without having it previously dissolved in alcohol. On the first day ζ was -27 millivolts, on the second day -30 millivolts. Motion again was very uniform.

Hydrochloric acid. The suspension was prepared with *m*-xylene which had previously been in contact with concentrated acid in aqueous solution for 1 to 2 days. On the first day ζ was -45 millivolts, on the second -26 millivolts, on the third -27 millivolts.

The increase of stability was not so pronounced as with picric acid, probably because of the limited solubility of hydrochloric acid in the organic solvent.

Potassium hydroxide. The *m*-xylene had been in contact with solid potassium hydroxide for 1 to 2 days, and had thus been allowed to become saturated.

One sample exhibited an anodic migration on the first day with $\zeta = -19$ millivolts, which changed over to cathodic migration on the second day with $\zeta = +32$ millivolts. On the third day only very few particles were detectable; $\zeta = +35$ millivolts. The particles showed a very pronounced Brownian motion.

Another sample showed a very poor motion of the particles on the first day, the sign of the motion being variable and uncertain. On the second day there were only a few particles visible, migrating cathodically with $\zeta = +15$ millivolts.

A third sample was prepared with 0.3 cc. of an alcoholic potassium hydroxide solution added to 10 cc. of the suspension. It had a potential of $+29$ millivolts on the first day, and on the second day there were scarcely any particles left.

From these observations the conclusion could be drawn that alkali tends to make the suspension unstable, by reversing the original negative charge into a positive one. That a slow reversal of sign is accompanied by instability is due to the fact that the charge must obviously pass through zero.

SUMMARY

This paper deals with cataphoresis in insulating media, polystyrene being chosen as the disperse phase.

In the theoretical part the validity for insulating media of the fundamental Helmholtz equation is discussed, and it is shown how the various factors in insulating liquids will affect the velocity of the particles. The main factor is the boundary potential, in connection with the thickness of the electrical double layer. It is indicated which value for this latter quantity can be expected in insulating liquids, and the way these values might affect the electrokinetic potential. The origins of this potential

(thermodynamic distribution, and ionic adsorption) are then dealt with, and their possible respective rôles in insulating liquids are considered.

In the experimental part the method is described by means of which suitable suspensions of polystyrene in a mixture of xylene and mineral oil can be prepared, and the different factors (concentration of ingredients, stabilizers) essential for producing the highest possible stability are enumerated. Two methods have been used to investigate cataphoresis. One consists in obtaining visual deposits of the resin on metal. The other, discussed more in detail, is a quantitative microscopic method. The trough used for the latter experiments is described, together with the working procedure and the computation of the electrokinetic potential from velocity data. Results of measurements follow, indicating an anodic motion and an order of magnitude of 30 millivolts for the potential. Finally the rôle of acidic and basic admixtures is investigated, showing that acids tend to stabilize the suspensions, whereas alkali hastens the coagulation, by reversing the negative charge of the particles into a positive one.

This work was begun at the Engineering Laboratory, Oxford University, and was finished at the Department of Chemical Technology, Imperial College, The University of London. The author is much indebted to Professor R. V. Southwell, F.R.S., and Professor A. C. Egerton, F.R.S., for facilities placed at his disposal.

REFERENCES

- (1) CHRISTOPHERSON, D. G., GEMANT, A., HOGG, A. H. A., AND SOUTHWELL, R. V.: *Proc. Roy. Soc. (London)* **168**, 351 (1938).
- (2) FALKENHAGEN, H.: *Electrolytes*. Clarendon Press, Oxford (1934).
- (3) FARMER, E. H.: *Annual Reports of the Chemical Society* **32**, 250 (1936).
- (4) See, for instance, GEMANT, A.: *Kolloidphysik*. Braunschweig (1925).
- (5) GEMANT, A.: *Liquid Dielectrics*. John Wiley and Sons, Inc., New York (1933).
- (6) GEMANT, A., AND SOUTHWELL, R. V.: British patent 434,994 (1935).
- (7) HUMPHRY, R. H., AND JANE, R. S.: *Trans. Faraday Soc.* **22**, 420 (1926).
- (8) LANTZ, E. A., AND PICKETT, O. A.: *Ind. Eng. Chem.* **22**, 1309 (1930).
- (9) WHITEHEAD, J. B., AND MAURITZ, F. E.: *Elec. Eng.* **56**, 465 (1937).

ANALOGUES OF ENTROPY

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INTRODUCTION

Entropy is commonly thought of as a very unique thermodynamic function with a most uncommon property of increasing all the time. It is also considered to be unique because it is so closely connected with the second law of thermodynamics, which forbids perpetual motion of the second kind by making the efficiency of a heat engine depend upon the limiting temperatures between which the engine works according to the formula

$$\text{Eff.} = 1 - T'/T''$$

where T' and T'' are the lower and upper limits of the working temperatures expressed in degrees absolute. This efficiency can become unity only if $T' = 0$, that is, if the condenser of the heat engine is at absolute zero.

It is the purpose of this communication to show that entropy is by no means unique in these two aspects, but that other common thermodynamic quantities share its "increasing" property and serve to define cycles the efficiency of which depends upon limiting values of forces other than temperature.

THE SECOND LAW OF THERMODYNAMICS

There have been many formulations (1 to 7) of the second law of thermodynamics and the end is not yet. The core of all of these formulations is that it is possible to represent the imperfect differential δq , the heat absorbed by a body, as the product of one point function and the differential of another, explicitly that

$$\delta q = TdS \quad (1)$$

where T is the absolute temperature and S is the entropy. This may therefore be taken as the import of the second law regardless of its specific formulation. The various properties of entropy follow directly from the application of this equation in the standard manner. The development will be indicated very briefly, simply for the purpose of comparison. For further details any textbook of thermodynamics may be consulted.

A heat engine works by using heat at high temperature to produce work, but at the same time it must discharge heat at a low temperature. In a typical heat engine the efficiency is defined as the ratio of the portion of high-temperature heat actually transformed into work to the total quantity of high-temperature heat used, all friction or other irreversible processes being avoided. Thus in the usual Carnot cycle, consisting of two isothermal and two adiabatic steps defined by the values T'' , T' , S' , S'' , respectively, as indicated in figure 1, the efficiency would be the ratio of the heat absorbed during the expansion at T'' less the heat discharged during the compression at T' to the heat absorbed at T'' :

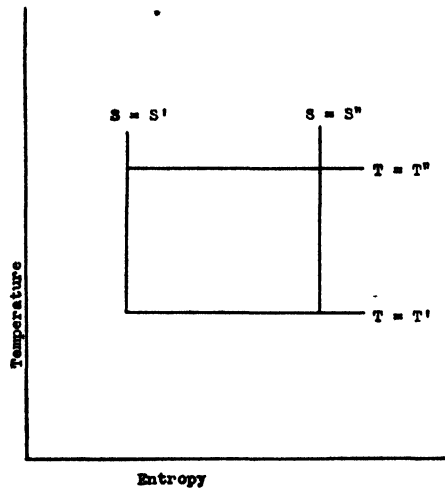


FIG. 1

$$\text{Eff.} = (Q'' - Q')/Q'' = W/Q'' = 1 - Q'/Q''$$

But, from equation 1,

$$Q' = T'(S'' - S') \quad \text{and} \quad Q'' = T''(S'' - S')$$

so that

$$Q'/Q'' = T'/T'' \quad \text{and} \quad \text{Eff.} = 1 - T'/T'' \quad \text{Q.E.D.}$$

To prove the increasing property of entropy it is necessary to prove that the work done during a reversible change of state is the maximum that can be done by a body in passing from state A to state B. This is done most expeditiously by observing that the work done by the body is

$$\delta w = \sum_1^s \delta w_r = \sum_1^s Y_r dy_r$$

since there will be in general a number of kinds of work performed and each of them will be expressed as the product of a generalized force, Y_r , and a

change in the conjugate coördinate, y_r . In fact, using the first law of thermodynamics and equation 1,

$$\begin{aligned} dE &= TdS - \delta w = TdS - \sum_1^s Y_r dy_r \\ &= -Y_0 dy_0 - \sum_1^s Y_r dy_r = -\sum_0^s Y_r dy_r \quad (2) \end{aligned}$$

since T and S enter formally on the same basis as the other generalized forces and coördinates. Here each $Y_r = -\partial E/\partial y_r$ and, since the condition for stable equilibrium is $\partial^2 E/\partial y^2 > 0$,

$$\partial Y_r/\partial y_r < 0$$

so that an increase in y_r is necessarily accompanied by a decrease in Y_r if no other changes take place simultaneously.

An irreversible change of state is one in which the initial decrease in Y_r , which causes local inequalities in its value, occurs so quickly that no time is allowed for the inequalities to become ironed out by a process of diffusion so that a definite value of Y_r might be assigned to the body as a whole. In such a case the force actually performing the work, which is the force active at the seat of the disturbance, is necessarily less during an irreversible than during a reversible change of state. Therefore the work done is less during an irreversible than during a reversible change of state.

Q.E.D.

Comparing two processes by means of which a body passes from state A to state B once reversibly and once irreversibly, it is clear that the change in value of all point functions for the body is the same in the two cases. In particular, ΔS is the same for both the reversible and the irreversible process as far as the working body is concerned. But the change of entropy of the environment is measured by $-Q/T$, where Q is the heat absorbed from the environment by the working body during the change of state. (By suitable mechanisms it can be arranged that the heat is supplied by the environment from a reservoir at constant temperature T .) But Q will be less in the irreversible case, because $Q = \Delta E + W$ and W is less in the irreversible case. Hence ΔS for the environment is *greater* in the irreversible case, and the total change in entropy of the system of body plus environment will be greater in the irreversible case. It is readily shown that this change in entropy for the reversible case is exactly zero. Hence, for the whole system,

$$\Delta S \geq 0$$

according as the process is irreversible or reversible. *Q.E.D.*

FUNCTIONS ANALOGOUS TO S

A trivial class of functions analogous to S will be the class defined by the formula

$$\delta q = y dx$$

where x may be not only S itself but some other function of S . This class arises from the general relationship between perfect and imperfect differentials. When the imperfect differential is multiplied by certain factors, known as integrating factors, it is changed into a perfect differential, that is, into an expression immediately integrable. Now if $dx = \delta q/y$ is immediately integrable, then so is

$$du = f(x)dx = \delta q f(x)/y$$

This simply says that an infinity of functions similar to S may be invented and used just as S is, with a corresponding change in the scale of temperature. There is no advantage in pursuing this point, since S itself is a most convenient function.

Returning to equation 2, it appears that formally there is no difference between the Ydy which stands for $-TdS$ and that which stands for $p dv$ or any other particular form of energy. Hence there should be analogies between S and all the other y 's and between T and all the other Y 's. As a typical case compare TdS and $p dv$. A cycle analogous to the Carnot cycle would be one composed of two isobars and two isometrics as shown in figure 2, defined by the values p'' , p' , v' , v'' . The efficiency of an engine performing this cycle would be defined by the ratio of the work transformed into heat to the total work in the high-pressure process. Following exactly the same development that was used with the Carnot cycle it is easy to prove that

$$\text{Eff.} = (W'' - W')/W'' = 1 - W'/W'' = 1 - p'/p''$$

Hence the efficiency of this engine will always be less than unity unless p' is zero. This corresponds to stating the second law of thermodynamics in the form "It is impossible to derive useful work from a substance by expanding it until its pressure is less than that of its surroundings." Compare with this the statement of Thomson (7): "It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of surrounding objects."

The argument is clearly general and applies to the efficiency of any engine working in a cycle to transform one sort of energy into another. The efficiency of the engine, defined in a manner analogous to the above, will never be unity unless the lower value of Y is zero, and, in fact, the

maximum efficiency is always given by $1 - Y'/Y''$. It follows that the y 's are all analogues of entropy and the Y 's of temperature.

It is important to stress the last point. It is a familiar statement that it is impossible to attain absolute zero (of temperature). A statement less familiar but just as true is that it is impossible to attain zero pressure. All forces such as pressure, temperature, surface tension, and so forth have absolute values measured from some absolute zero, but in all cases the absolute zero of such parameters is attainable only asymptotically, that is, never. All such forces are measured by balancing them against other forces to which arbitrary values have been assigned.

It remains to be seen to what extent and under what conditions the quantities y , volume, for example, exhibit properties analogous to the increasing property of entropy. For this purpose the *whole system* of

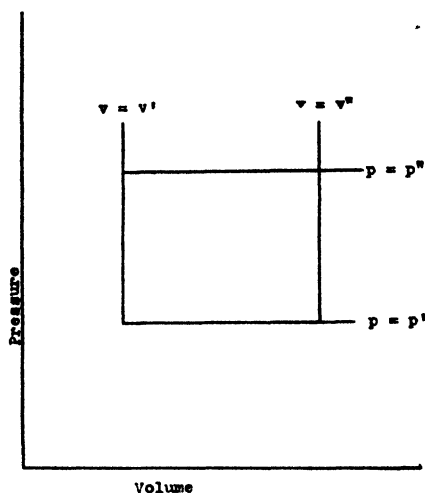


FIG. 2

body plus environment must be taken into account. If we consider the system to be isolated, which may be done if actual experimental conditions are extrapolated to ideal ones or if the system is the whole physical universe, then the energy of that system is fixed. Let (') refer to the working body, (") to the environment, and unaccented symbols to the whole system. Then in any change of state, reversible or not,

$$dE = dE' + dE'' = 0$$

Further

$$dE' = \sum \delta e_r'; \quad dE'' = \sum \delta e_r''$$

Various forms of energy may be exchanged between body and environment. Let the body undergo a change of state from A' to B' involving

any suitable changes in the independent variables y_r' , once reversibly and once irreversibly. This will induce a corresponding change of state (A'' to B'') in the environment such that $\Delta E'' = -\Delta E'$ and may result in various changes in the y_r'' . In the reversible case, the final state B'' will be fixed by the final state of the body, B' . In the irreversible case the state B'' will depend upon just how the change of state is caused to take place, and it is possible in general to make B'' for the irreversible case identical with B'' for the reversible case *except for a difference in the final value of one of the parameters y''* . Further, since the y 's are all additive for body and environment so that

$$\Delta y_r = \Delta y_r' + \Delta y_r''$$

and since it is readily shown that in the reversible case $\Delta y_r = 0$ for all values of r , it follows that in the irreversible case there will be a net change in at least one of the y_r .

In the usual proof of the increasing property of entropy it is implicitly or explicitly assumed that the final state of the environment, B'' , in the reversible case differs from that in the irreversible case solely in the value of the particular y'' which stands for entropy. This is obviously not a necessary condition, although it is just as obviously a sufficient one. The difference might equally well have been attributed to a difference in the value of the y'' that stands for volume or for any other coördinate. In the summary of the classical development given earlier in this paper it was stated casually that the change in entropy of the environment is measured by $-Q/T$, suitable mechanisms being employed to ensure that the heat is supplied from a reservoir at constant temperature. This means that a deliberate choice has been made of B'' , a choice in which entropy alone shall have been altered. Actually the choice might have been made in as many ways as there are kinds of y'' .

Assume that the irreversibility arose from a change of state involving the s^{th} type of energy. Then, by the argument used in development of the early part of this paper, $\delta \epsilon_s'$ is greater for the irreversible than for the reversible change of state. Since dE' is the same for both changes, at least one other form of energy, say the n^{th} , must have suffered a change $\delta \epsilon_n'$, which is less for the irreversible than for the reversible change. The corresponding change in ϵ_n'' for the environment, $\delta \epsilon_n''$, will therefore be greater for the irreversible than for the reversible change and

$$dy_n'' = -\delta \epsilon_n / Y_n''$$

will be less for the irreversible change. Hence dy_n , which is the sum of dy_n' and dy_n'' , will always be less for an irreversible than for a reversible change. Therefore the variable y_n will have suffered a net *decrease* every time there is any irreversibility. Applying this to the specific case of entropy we note that

$$TdS = -Y_0 dy_0, \quad T = Y_0, \quad dS = -dy_0$$

Hence if the irreversibility is to be measured as a net change in entropy, it will be found that entropy will always *increase*. If, on the other hand, some other variable had been selected, say volume, a net decrease in volume would have been a measure of irreversibility. *Any one of the usual extensive energetic factors might serve equally well to detect irreversibility and might be regarded as having the property of not being conserved but of tending to an extreme value.*

A further consequence is that it is not necessary to restrict the lack of identity of the two final states B'' of the environment to a difference in only one of the y'' . Two or more might be considered to have altered permanently.

These considerations seem to have been overlooked in textbooks and treatises on thermodynamics, and a great emphasis upon the uniqueness of entropy has been the consequence. There is no harm, but rather a great convenience, in measuring irreversibility always in terms of one parameter such as entropy or a derived function such as free energy, so long as it is realized that such measurement tacitly implies that all other extensive properties of the universe, including volume in particular, are maintained at fixed values. If the isolated system is so arranged that this implication accords with the particular experimental set-up, then it is true that entropy alone increases during an irreversible process. As regards the whole material universe, however, we have no information upon any restriction upon its volume and therefore no certainty that its entropy is forever increasing.

SUMMARY

It has been shown that entropy and temperature are not unique but have properties analogous to other extensive and intensive energy factors, respectively. In particular, it is shown that the entropy is not the only function that may tend to an extreme value for the universe because of irreversibility.

REFERENCES

- (1) CARNOT: Reflections on the Motive Power of Heat. (1824).
- (2) CLAUSIUS: Pogg. Ann. **79**, 376, 500 (1850).
- (3) HAZLEHURST: J. Chem. Education **9**, 1087 (1932).
- (4) LEWIS, G. N.: J. Am. Chem. Soc. **53**, 2578 (1931).
- (5) LEWIS AND RANDALL: Thermodynamics, p. 127. McGraw-Hill Book Company, New York (1923).
- (6) PLANCK: Treatise on Thermodynamics, translated by A. Ogg. Longmans, Green and Company, New York (1927).
- (7) THOMSON: Mathematical and Physical Papers, Vol. I, p. 174. Cambridge University Press, Cambridge (1911).

STUDIES ON AGING AND COPRECIPITATION. XXVIII

ADSORPTION OF DIVALENT IONS ON AND COPRECIPITATION WITH ORTHO FERRIC HYDROXIDE IN AMMONIACAL MEDIUM¹

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In a previous paper (4) the adsorption of the ammonio copper ion on and coprecipitation with ortho ferric hydroxide has been studied, and a condensed review of the literature on the adsorption and coprecipitation of divalent ions from ammoniacal medium has been given. In the present work the studies have been extended to the adsorption and coprecipitation of zinc, nickel, cobalt, manganese, magnesium, and calcium.

MATERIALS

Most of the reagents and salts used were of c.p. quality. For the purity of ferric chloride and ammonia the reader is referred to a previous study (4).

ANALYTICAL PROCEDURES

Zinc was determined by the ferrocyanide method, using the directions of Kolthoff and Pearson (5). In a few experiments zinc was determined by the oxine method, following the directions of Fleck and Ward (1). The method yielded results that checked to 0.3 per cent when analyzing 0.1 millimole of zinc, while an ammonium chloride concentration as great as 1 molar had no effect. *Nickel* was determined by the cyanide method, following the directions of Kolthoff and Griffith (3). *Cobalt* was determined by the oxine method as given by Fleck and Ward (1). The precipitated oxine salt was determined bromometrically, using the procedure given by Kolthoff and Furman (2). The method yielded results that checked. *Manganese* was determined by the induced oxidation method of Lang (7). Large amounts of chloride interfere in this determination, while the presence of ammonium salts has no effect. Chloride was re-

¹ This article is based on a thesis submitted by L. G. Overholser to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1938.

moved by adding sulfuric acid and heating until heavy white fumes were evolved. *Magnesium* was determined gravimetrically by the oxine method, following the directions of Fleck and Ward (1). Magnesium is quantitatively precipitated from a solution whose pH is between 9.5 and 12.0. In our determinations the ratio of ammonia to ammonium salts was 5 to 8, which gave a pH of approximately 10 as shown by colorimetric determinations. Results were obtained that checked to within 0.5 per cent by carefully regulating the ammonia concentration. *Calcium* was determined by precipitating the oxalate and determining it volumetrically

TABLE 1
Adsorption of zinc on ferric hydroxide
 Final concentration of zinc was 0.019 ± 0.002 molar

CONCENTRATION OF AMMONIA	CONCENTRATION OF AMMONIUM CHLORIDE	ADSORPTION	ADSORPTION PER GRAM OF Fe_2O_3
<i>molar</i>	<i>molar</i>	<i>per cent</i>	<i>millimoles</i>
0.234	0.250	12.8	1.43
0.234	0.500	8.4	0.94
0.234	0.750	6.9	0.77
0.234	1.00	4.9	0.55
0.234	1.25	4.9	0.55
0.234	1.50	4.2	0.47
0.234	1.75	3.2	0.35
0.733	0.077	12.4	1.38
0.733	0.250	6.5	0.72
0.733	0.500	3.4	0.38
0.733	0.750	2.1	0.23
0.733	1.00	0.9	0.10
0.733	1.25	0.8	0.09
0.733	1.50	1.1	0.12
1.230	0.077	9.2	1.02
1.230	0.250	5.3	0.59
1.230	0.500	2.8	0.31
1.230	0.750	0.9	0.10
1.230	1.00	0	0

with permanganate. *Ammonia* was determined by the ordinary distillation method, using sodium hydroxide. The evolved ammonia was determined by the hypochlorite method of Kolthoff and Stenger (6).

EXPERIMENTAL RESULTS

Adsorption experiments on ferric hydroxide precipitated at room temperature

The entire amount of ammonia was added rapidly with constant stirring to 25 ml. of 0.1 *M* ferric chloride, 10 ml. of an approximately 0.2 *M* solution of the metal salt whose adsorption was being studied was added, and the suspension was diluted to 100 ml. with distilled water. The suspension was allowed to stand for 40 min. at room temperature with occasional shak-

TABLE 2

*Adsorption of nickel and cobalt on ferric hydroxide*Final concentration of nickel was 0.018 ± 0.002 molar; of cobalt 0.017 ± 0.002 molar

CONCENTRATION OF AMMONIA	CONCENTRATION OF AMMONIUM CHLORIDE	ADSORPTION		ADSORPTION PER GRAM OF Fe_2O_3	
		Ni	Co	Ni	Co
<i>molar</i>	<i>molar</i>	<i>per cent</i>	<i>per cent</i>	<i>millimoles</i>	<i>millimoles</i>
0.250	0.077	20.3		2.03	
0.500	0.077	15.4		1.53	
0.750	0.077	12.5		1.25	
0.900	0.077	11.2		1.12	
1.25	0.077	9.2		0.91	
1.50	0.077	7.4		0.74	
2.00	0.077	5.9		0.59	
0.250	0.500	9.6		0.95	
0.250	1.00	6.0	24.3	0.59	2.48
0.250	1.50	4.7	19.7	0.47	2.01
0.250	2.00	3.2	16.5	0.32	1.69
0.900	0.500	3.1	20.2	0.31	2.06
0.900	1.00	1.3	15.2	0.13	1.56
0.900	1.50	0.6	10.4	0.06	1.06
0.900	2.00	0.4	9.5	0.04	0.97
1.50	0.500	1.6	17.5	0.16	1.79
1.50	1.00	0.8	11.6	0.08	1.19
1.50	2.00	0.3	8.2	0.03	0.83
2.00	1.00	0	10.4	0	1.06
2.00	2.00	0	6.9	0.01	0.70

TABLE 3

Adsorption of manganese on ferric hydroxide

MANGANESE CONCENTRATION*	CONCENTRATION OF AMMONIA	CONCENTRATION OF AMMONIUM CHLORIDE	ADSORPTION	ADSORPTION PER GRAM OF Fe_2O_3
	<i>molar</i>	<i>molar</i>	<i>per cent</i>	<i>millimoles</i>
1	0.003	1.00	8.1	0.83
1	0.01	1.00	16.4	1.70
1	0.05	1.00	30.7	3.18
1	0.10	1.00	38.1	3.95
1	0.10	1.50	33.8	3.50
1	0.10	2.00	30.2	3.12
1	0.20	2.00	33.0	3.42
2	0.003	0.250	45.9	0.47
2	0.003	0.500	36.3	0.37
2	0.003	1.00	27.2	0.28
2	0.003	1.50	22.3	0.23
2	0.003	2.00	20.3	0.21

* 1 refers to a final concentration of manganese of 0.016 ± 0.003 molar; 2 refers to a final concentration of manganese of 0.0014 ± 0.0003 molar.

ing and then filtered. An aliquot portion of the filtrate was analyzed for the metal by the appropriate procedure. Where required, ammonium chloride was added prior to the addition of the metal salt solution. The final concentration of ammonia was found from the total amount added by subtracting the amount required for the precipitation of the ferric chloride, the amount reacting with the metal salt, and, in the case of zinc, nickel, and cobalt, the amount required to keep the metallic ion in solution as the ammonio ion. The results on the adsorption of zinc, nickel, cobalt, manganese, calcium, and magnesium are given in tables 1 to 4, inclusive.

TABLE 4

*Adsorption of magnesium and calcium on ferric hydroxide**

Final concentration of magnesium was 0.020 ± 0.0015 molar;
of calcium 0.018 ± 0.002 molar

CONCENTRATION OF AMMONIA	CONCENTRATION OF AMMONIUM CHLORIDE	ADSORPTION		ADSORPTION PER GRAM OF Fe_2O_3	
		Mg	Ca	Mg	Ca
<i>molar</i>	<i>molar</i>	<i>per cent</i>	<i>per cent</i>	<i>millimoles</i>	<i>millimoles</i>
0.004	0.077	5.2	5.1	0.55	0.51
0.004	0.250	2.5		0.27	
0.004	0.500	0.8	2.5	0.09	0.25
0.004	1.00	0.4	1.2	0.04	0.12
0.004	1.50	0.6	0.9	0.06	0.09
0.004	2.00	0	0.2	0	0.02
0.500	0.077		16.9		1.69
0.900	0.077		19.0		1.90
0.900	0.500	14.6		1.56	
0.900	1.00	9.3	12.2	0.99	1.22
0.900	2.00	5.5	9.6	0.59	0.96
1.80	0.077		20.8		2.08
1.80	0.500				
1.80	1.00	10.4	13.5	1.11	1.35
1.80	2.00	6.7	10.6	0.71	1.06

* In the magnesium experiments the ferric hydroxide was aged for 1 hr. prior to the addition of magnesium. Calcium was added immediately after the precipitation of the ferric hydroxide.

Effect of sodium sulfate on the adsorption of zinc

From the results reported in table 1 it is seen that the adsorption of zinc was greatly reduced and in some instances entirely eliminated by the presence of large amounts of ammonium salts. It was of interest to determine the effect of other salts on the adsorption; accordingly several experiments were performed in the presence of varying amounts of sodium sulfate. With all other experimental conditions identical, the presence of 0.5 *M* sodium sulfate reduced the adsorption of zinc from 11.4 to 7.8 per cent, while 1.0 *M* sodium sulfate reduced it to 5.9 per cent. Ammonium chloride present in the above concentrations reduced the adsorption to less

than 1 per cent. Kolthoff and Moskovitz (4) have reported similar results in studies of the effect of potassium chloride and other alkali salts on the adsorption of copper.

Adsorption isotherm of zinc and nickel

Sufficient ammonia was added at room temperature to 25 ml. of 0.1 *M* ferric chloride to give an excess of 0.1 mole after diluting to 100 ml., varying amounts of either zinc sulfate or nickel chloride were added immediately after precipitation, and the suspension was allowed to stand for 40 min. at room temperature with occasional shaking prior to filtration. The results are given in table 5 with the calculated values obtained from the Freundlich adsorption equation

TABLE 5
Adsorption isotherm of zinc and nickel in 1 M ammonia

FINAL CONCENTRATION		ZINC ADSORBED	NICKEL ADSORBED	NUMBER OF MILLIMOLES PER GRAM OF Fe ₂ O ₃			
Zinc	Nickel			Zinc		Nickel	
				Found	Calculated	Found	Calculated
molar	molar	per cent	per cent				
0.00342	0.00360	32.3	27.5	0.81	0.82	0.67	0.66
0.00782	0.00809	22.0	17.9	1.09	1.08	0.87	0.85
0.0172	0.0176	14.4	10.8	1.43	1.44	1.06	1.05
0.0316	0.0320	9.9	7.1	1.72	1.81	1.22	1.27
0.0463	0.0465	7.9	5.4	1.97	2.10	1.32	1.43
0.0663	0.0664	6.0	4.1	2.09	2.42	1.42	1.61
0.0962	0.0956	4.3	3.3	2.13	2.79	1.62	1.82

$$\frac{X}{m} = ac^{1/n}$$

in which X/m represents the number of millimoles of zinc or nickel adsorbed per gram of ferric oxide and a is a constant, which was found to be 7.16 for zinc and 3.98 for nickel, while $1/n$ was found equal to 0.41 for zinc and 0.34 for nickel. At the higher metal concentrations the experimental values were smaller than the calculated ones, in agreement with the results reported by Kolthoff and Moskovitz (4), who attributed the deviation to a repression of the adsorption of copper by the ammonium salts formed by the interaction of the copper salt with ammonia.

The form in which zinc is adsorbed

Two different types of experiments were performed to determine whether the zinc was adsorbed as ammonio or as aquo ion. In one set the ammonia was added at room temperature to a mixture of 25 ml. of 0.1 *M* ferric chloride and 25 ml. of 0.09 *M* zinc sulfate and the suspension was diluted to 100 ml. After 15 min. of standing, the supernatant liquid was

removed and analyzed for zinc. The precipitate was washed with conductivity water until the washings gave no test for ammonia with Nessler's reagent and was then analyzed for zinc and ammonia. The results showed that, whereas the amount of zinc in or on the precipitate ranged from 0.14 to 0.17 millimole, only 0.01 millimole of ammonia was present, indicating that the adsorption was not one of zinc ammonia ions.

During the washing process in the above procedure zinc was slowly removed from the precipitate and was still being washed out after a negative test for ammonia was obtained. To preclude any effect that the washing may have had, the following procedure was also utilized: 25 ml. of a solution of zinc ammonio complex of known zinc and ammonia content was added to 25 ml. of a freshly prepared ferric hydroxide suspension of known ammonia content. The suspension was diluted to 100 ml. with ammonia-free water and centrifuged after 40 min. of standing at room temperature. The supernatant liquid was analyzed for both zinc and ammonia, and the amount of each adsorbed was calculated from these results and the original composition of the solution. It was found that 0.7 millimole of zinc but only 0.2 millimole of ammonia had been adsorbed. These results, in agreement with the preceding ones, show conclusively that the zinc was adsorbed not as the ammonio ion but probably as the aquo ion or the anhydrous zinc ion.

Adsorption on ferric hydroxide precipitate formed at 98°C.

Twenty-five milliliters of 0.1 *M* ferric chloride was heated to 98°C., the iron precipitated with ammonia at this temperature, and the suspension cooled to room temperature immediately. The adsorption of the different metals was then determined in a manner analogous to that of the experiments in which the precipitate was formed at room temperature. It was found that in the case of nickel and magnesium the amount of metal adsorbed on the precipitate formed at 98°C. was about one-half of that adsorbed on the precipitate formed at room temperature. For cobalt the difference was less, but the adsorption of this metal increases markedly with the time of standing, making a true comparison difficult. More will be said of this behavior of cobalt in a subsequent paper. Kolthoff and Moskovitz (4) aged the precipitate for 1 min. at 98°C., following the precipitation at this temperature, then cooled and found about three and five-tenths to four times as much copper adsorbed on the precipitate formed at room temperature as on that formed at 98°C. The greater difference in the case of copper is explained by the fact that upon heating the precipitate even for only 1 min. a pronounced aging occurs.

Coprecipitation experiments at room temperature and at 98°C.

The ammonia was added at room temperature to a mixture consisting of 25 ml. of 0.1 *M* ferric chloride, 25 ml. of approximately 0.08 *M* metal

salt, and varying amounts of ammonium chloride (where required). The suspension was diluted to 100 ml. with water, allowed to stand at room temperature for the designated period of time, and filtered; the filtrate

TABLE 6
*Coprecipitation of zinc**

CONCENTRATION OF AMMONIA	CONCENTRATION OF AMMONIUM CHLORIDE	TEMPERATURE OF COPRECIPITATION	COPRECIPITATION	COPRECIPITATION PER GRAM OF Fe_2O_3
<i>molar</i>	<i>molar</i>		<i>per cent</i>	<i>millimoles</i>
0.90	0.077	Room temperature	17.6	1.98
0.90	0.098	98°C.	17.7	1.99
0.90	1.75	Room temperature	2.4	0.27
0.90	1.75	98°C.	1.1	0.12
1.81	0.077	Room temperature	12.5	1.40
1.81	0.098	98°C.	11.2	1.26
1.81	1.75	Room temperature	0.4	0.04
1.81	1.75	98°C.	0	0.01

* From 10 to 15 min. elapsed between precipitation and filtration. The final concentration of zinc was 0.020 ± 0.002 molar.

TABLE 7
Coprecipitation of nickel and cobalt

Final concentration of nickel was 0.017 ± 0.003 molar;
of cobalt 0.017 ± 0.002 molar

CONCENTRATION OF AMMONIA	CONCENTRATION OF AMMONIUM CHLORIDE	TEMPERATURE OF COPRECIPITATION	COPRECIPITATION		COPRECIPITATION PER GRAM OF Fe_2O_3	
			Ni	Co	Ni	Co
<i>molar</i>	<i>molar</i>		<i>per cent</i>	<i>per cent</i>	<i>millimoles</i>	<i>millimoles</i>
0.250	0.077	Room temperature	28.3		2.82	
0.500	0.077	Room temperature	21.1		2.10	
0.900	0.077	Room temperature	14.7		1.47	
0.900	0.097	Room temperature	13.4*		1.34*	
0.900	0.097	98°C.	18.7*		1.86*	
0.900	0.500	Room temperature		27.2		2.76
0.900	1.00	Room temperature	2.4	17.9*	0.24	1.82*
0.900	1.00	98°C.		19.7*		2.00*
0.900	1.50	Room temperature	1.3	16.2	0.12	1.64
0.900	2.00	Room temperature	0.6	12.3	0.06	1.25
1.50	0.077	Room temperature	10.1		1.00	
1.50	0.50	Room temperature		19.5		1.98
1.50	1.00	Room temperature		15.2		1.54
1.50	2.00	Room temperature		7.1		0.72
2.00	0.077	Room temperature	7.9		0.78	
2.00	1.00	Room temperature	0.3	10.5	0.03	1.07
2.00	1.50	Room temperature	0.1		0.01	
2.00	2.00	Room temperature	0	6.6	0	0.67

* From 5 to 8 min. elapsed between precipitation and filtration. In all other cases this period was 40 min.

TABLE 8
Coprecipitation of manganese at room temperature

MANGANESE CONCENTRATION*	CONCENTRATION OF AMMONIA	CONCENTRATION OF AMMONIUM CHLORIDE	COPRECIPITATION	COPRECIPITATION PER GRAM OF Fe ₂ O ₃
	<i>molar</i>	<i>molar</i>	<i>per cent</i>	<i>millimoles</i>
1	0.003	1.00	11.2	1.16
1	0.003	2.00	8.2	0.85
1	0.05	1.00	40.1	4.12
1	0.10	1.00	47.5	4.88
1	0.10	1.50	41.7	4.29
1	0.10	2.00	38.2	3.92
1	0.20	2.00	43.8	4.50
2	0.003	0.25	56.6	0.60
2	0.003	0.50	45.2	0.47
2	0.003	1.00	33.5	0.35
2	0.003	1.50	29.0	0.30
2	0.003	2.00	23.9	0.25

* 1 refers to a final concentration of manganese of about 0.015 ± 0.004 molar, and 2 to a final concentration of 0.0013 ± 0.0003 molar. The time between precipitation and filtration was from 6 to 10 min.

TABLE 9
*Coprecipitation of magnesium and calcium**
Final concentration of magnesium was 0.019 ± 0.002 molar;
of calcium 0.018 ± 0.002 molar

CONCENTRA- TION OF AMMONIA	CONCENTRA- TION OF AMMONIUM CHLORIDE	TEMPERATURE OF COPRECIPITATION	COPRECIPITATION		COPRECIPITATION PER GRAM OF Fe ₂ O ₃	
			Mg	Ca	Mg	Ca
<i>molar</i>	<i>molar</i>		<i>per cent</i>	<i>per cent</i>	<i>millimoles</i>	<i>millimoles</i>
0.001	0.077	Room temperature	4.0		0.41	
0.001	0.50	Room temperature	0.9		0.09	
0.001	1.00	Room temperature	0.9		0.09	
0.001	1.50	Room temperature	0.2		0.02	
0.001	2.00	Room temperature	0.3		0.03	
0.003	0.097	98°C.	6.7		0.70	
0.003	0.50	98°C.	1.2		0.12	
0.003	1.00	98°C.	0.3		0.03	
0.003	1.50	98°C.	0		0	
0.003	2.00	98°C.	0		0	
0.008	0.077	Room temperature		6.4		0.64
0.008	1.00	Room temperature		2.5		0.24
0.008	2.00	Room temperature		1.1		0.11
0.900	0.077	Room temperature		20.8		2.07
0.900	1.00	Room temperature	16.5	12.9	1.72	1.29
0.900	1.00	98°C.	12.7	7.7	1.32	0.77
0.900	2.00	Room temperature	9.9		1.08	
0.900	2.00	98°C.	8.3		0.86	
1.80	0.077	Room temperature		22.9		2.28
1.80	1.00	Room temperature	19.8		2.07	
1.80	1.00	98°C.	13.7		1.43	
1.80	2.00	Room temperature	13.1		1.37	
1.80	2.00	98°C.	9.3		0.97	

* The time between precipitation and filtration was 40 min

was analyzed for the metal being studied. (See tables 6, 7, 8, and 9.) In the experiments in which the coprecipitation was performed at 98°C. the mixture of ferric chloride, metal salt, etc. was heated to 98°C. prior to the addition of the ammonia and was cooled to room temperature immediately thereafter.

Coprecipitation at low concentration of the metals

The concentration of the metals was approximately 0.002 *M*, that of the iron 0.025 *M*. The experiments were carried out at room temperature, and the precipitates were filtered after standing for 40 min. The results are given in table 10.

TABLE 10
Coprecipitation at low concentrations at room temperature

METAL	CONCENTRATION OF AMMONIA	CONCENTRATION OF AMMONIUM CHLORIDE	COPRECIPITATION	COPRECIPITATION PER GRAM OF Fe ₂ O ₃
	molar	molar	per cent	millimoles
Zinc .	2.00	2.00	0.3	0.003
Nickel . . .	2.00	2.00	5.0	0.048
Magnesium. . . .	0.003	2.00	3.6	0.037
Calcium.	0.003	2.00	0.7	0.006

Coprecipitation of a mixture of zinc and calcium

The experiments were carried out at room temperature, using a concentration for zinc and calcium of approximately 0.02 *M* and an iron concentration of 0.025 *M*. At ammonia and ammonium chloride concentrations of 0.900 and 0.076 *M*, respectively, the per cent of zinc coprecipitated was 9.2, as compared to 17.7 per cent when zinc alone was coprecipitated with iron. Under these conditions the per cent of calcium coprecipitated was 30.3, as compared to 21.0 when coprecipitated in the absence of zinc. In 0.900 *M* ammonia and 1.00 *M* ammonium chloride the per cent of zinc coprecipitated in the presence of calcium was 1.5, as against 3.2 without calcium. The per cent of calcium coprecipitated was 15.3 in the presence of zinc, 13.1 without zinc. The decrease in the amount of zinc coprecipitated in the presence of calcium was anticipated, since in this case part of the adsorptive surface was covered with calcium, leaving less available for the zinc. The increase in the coprecipitation of calcium in the presence of zinc, however, is not understood. It is peculiar that the amount of calcium coprecipitated from the mixture is equal to the amount of calcium coprecipitated in the absence of zinc plus the amount of zinc coprecipitated in the presence of calcium.

DISCUSSION

1. From the first four tables and figure 1 it is seen that the adsorption of the various cations decreases with increasing ammonium chloride con-

centration. The ammonium salts have two effects: (a) the ammonium ion has a replacing effect upon the other adsorbed ions; (b) the ammonium ions decrease the hydroxide-ion concentration of the solution. The adsorption of the various metals is due to a primary adsorption of hydroxide ions and a secondary adsorption of the cations. The primary adsorption of hydroxide ions decreases with decreasing hydroxide-ion concentration and, consequently, the secondary adsorption of cations also. That the replacing effect of the ammonium ions is not solely responsible for the decrease of the adsorption is apparent from a comparison of the effects of ammonium and sodium salts upon the adsorption of zinc (and of potassium upon copper (4)). Sodium ions have less effect than ammonium

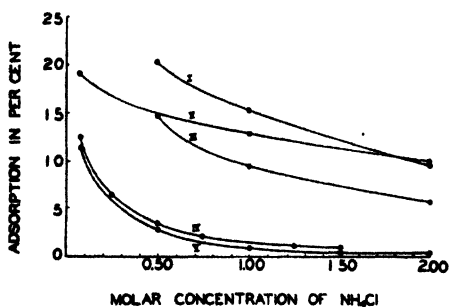


FIG. 1

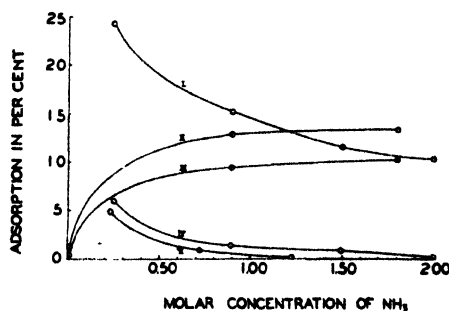


FIG. 2

FIG. 1. Effect of ammonium chloride concentration on the adsorption of the various metals. I, cobalt; II, calcium; III, magnesium; IV, zinc; V, nickel. Concentration of ammonia present: I, II, III, and V, 0.90 *M*; IV, 0.73 *M*.

FIG. 2. Effect of concentration of ammonia on the adsorption of the various metals. I, cobalt; II, calcium; III, magnesium; IV, nickel; V, zinc. The concentration of ammonium chloride was 1.00 *M* in all cases.

ions, as they do not decrease the hydroxide-ion concentration in the solution.

2. When the effect of ammonia concentration upon the adsorption is plotted we notice that the adsorption of calcium and magnesium increases with increasing ammonia concentration, but that the adsorption of zinc, nickel, and cobalt (and copper (4)) decreases. As an increasing ammonia concentration causes an increase of the hydroxide-ion concentration in the solution, an increase of the adsorption was to be expected and was actually found in the case of calcium and magnesium (and manganese). At the ammonia concentrations used, calcium and magnesium are mainly in solution as aquo ions. This is no longer true for zinc, nickel, and cobalt (and copper). In agreement with results reported by Miss Levy (8) we found that zinc is adsorbed not in the form of the ammonio ion but probably as aquo ion. The decrease, with increasing ammonia concentration,

of the adsorption of metals that form stable ammonio complexes—zinc, nickel, cobalt, copper—then is explained by the fact that the concentration of the aquo ions in solution decreases.

3. The Freundlich isotherm $X = ac^{1/n}$ holds over a wide range of concentrations for the adsorption of zinc and nickel (and copper) from 1 *M* ammonia.

4. All factors that affect the adsorption of the various metals affect their coprecipitation with ortho ferric hydroxide in a similar way. A comparison of the amounts of the metal ions adsorbed and coprecipitated under varying conditions is given in table 11. When comparing the

TABLE 11
Comparison of adsorption and coprecipitation

METAL	ADSORPTION ON THE PRECIPITATE FORMED AT ROOM TEMPERATURE	COPRECIPITATION AT ROOM TEMPERATURE	COPRECIPITATION AT 98°C.	ADSORPTION ON THE PRECIPITATE FORMED AT 98°C.
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Zinc.	11.9	17.6	17.7	
Nickel.	9.3	13.4	18.7	5.7
Nickel.	20.3	28.3		
Nickel.	5.9	7.9		
Cobalt.	10.9	17.9	19.7	7.4
Cobalt.	9.5	12.3		
Cobalt.	17.5	19.5		
Cobalt.	20.2	27.2		
Magnesium	9.3	16.5	12.7	4.4
Magnesium	6.7	13.1	9.3	
Calcium.	12.2	12.9	7.7	
Calcium.	19.0	20.8		
Calcium.	20.8	22.9		

figures in a horizontal row the final composition of the solution was always the same.

It is seen that at room temperature the amount of metal coprecipitated was somewhat greater than the amount adsorbed when the metal was added immediately after the precipitation of the hydroxide. This is in agreement with the results obtained with copper (4). Ferric hydroxide at room temperature precipitates in an amorphous form—with a large surface development. After its formation the hydroxide undergoes aging (agglomeration of primary particles, polymerization), which results in a decrease of its surface and therefore its adsorptive properties. When the

metal is coprecipitated with the hydroxide it can be adsorbed on the entire surface, whereas when added after the precipitation it does not necessarily have access to the entire internal surface because of the aging that may have occurred. Consequently one would expect the coprecipitation to be greater, but the difference found was not great. Apparently, most of the surface of the amorphous precipitate formed at room temperature is exposed to the solution.

When formed at 98°C. a product possessing more crystalline properties separates than at room temperature. Thus the adsorption on the hydroxide formed at 98°C. would be expected to be less than on the product formed at room temperature. Actually this was found, the adsorption being roughly one-half as much on the product formed at 98°C. as on that formed at room temperature.

Whereas the temperature of precipitation has a marked effect on the adsorption, very little difference in the amount of coprecipitation was found at the two different temperatures. In the case of zinc the amount coprecipitated was nearly equal at the two temperatures; for nickel and cobalt it was somewhat greater at 98°C.; and for calcium and magnesium it was smaller at 98°C. Since the precipitate formed at 98°C. already portrays crystalline properties, adsorption during the growth of the particles may occur, resulting in an occlusion. This explains why the coprecipitation is much greater than the adsorption when precipitation is carried out hot, whereas at room temperature coprecipitation and adsorption are of the same order of magnitude.

A close comparison of the coprecipitation data at room temperature and at 98°C. is somewhat complicated by the fact that the amounts of coprecipitated zinc, nickel, and cobalt (and copper) at 98°C. increase markedly when the precipitate is left in contact with the solution. In a subsequent paper it will be shown that the rate of increase of nickel and cobalt on standing is greater than that of zinc. This explains the fact that the coprecipitation of nickel and cobalt at 98°C. was found to be greater than at room temperature, while that of zinc was the same at both temperatures. In the case of magnesium little change was noted in the coprecipitation on standing at 98°C. From the results reported one would conclude, then, that the actual coprecipitation is slightly greater at room temperature than at 98°C.

The amount of calcium found coprecipitated at 98°C. was found to decrease markedly with the time of standing. Thus, it is not surprising to find that the amount of calcium coprecipitated at 98°C. is smaller than at room temperature (table 11), as some time elapses before the precipitate and solution are cooled from 98°C. to room temperature.

From the analytical viewpoint it may be said that the results show that zinc, nickel, magnesium, and calcium may be separated satisfactorily from iron by a single precipitation by employing the proper ammonia

and ammonium chloride concentrations. Cobalt and manganese cannot be satisfactorily separated from iron by this method. A quantitative separation of zinc or nickel from iron is effected with a high concentration (1.5 to 2.0 *M*) of both ammonia and ammonium chloride. Magnesium or calcium may be separated from iron by using an extremely low ammonia (0.003 *M*) and a high ammonium chloride concentration (1 to 2 *M*). A mixture of members of the two different groups such as zinc and magnesium can not be separated by a single precipitation, since a high ammonia concentration would give a separation of zinc but not of calcium and a low ammonia concentration the opposite effect. The temperature of precipitation of the hydroxide has little effect for zinc, better results are obtained at low temperatures for nickel, and more favorable results at high temperatures for calcium and magnesium.

SUMMARY

1. The effect of the concentration of ammonia and ammonium chloride upon the adsorption of the metals on and coprecipitation with ortho ferric hydroxide has been determined. The adsorption and coprecipitation of zinc, nickel, and cobalt decreases with increasing ammonia and ammonium chloride concentrations, while that of magnesium, calcium, and manganese decreases with increasing ammonium chloride concentrations but increases with increasing ammonia concentrations.

2. The adsorption and coprecipitation of zinc and nickel was found to be very small or entirely eliminated if the ammonia concentration was 0.9 *M* or greater and the ammonium chloride concentration was 1 to 2 *M*. The adsorption and coprecipitation of cobalt was appreciable even at an ammonia and ammonium chloride concentration of 2 *M*. The adsorption and coprecipitation of magnesium and calcium was negligibly small at an ammonia concentration of 0.005 *M* or less and an ammonium chloride concentration of 1.5 to 2 *M*. The adsorption and coprecipitation of manganese was even large at an extremely low ammonia and high ammonium chloride concentration.

3. The adsorption of zinc and nickel follows the Freundlich adsorption isotherm.

4. Zinc has been found to be adsorbed as the aquo ion and not as the complex ammonio ion.

5. The coprecipitation of the metals at room temperature is only slightly greater than their adsorption when the metals are added immediately after precipitation of the ferric hydroxide.

6. The amounts of zinc, nickel, and cobalt coprecipitated at 98°C. were found to be only slightly greater than those coprecipitated at room temperature. The amounts of magnesium and calcium coprecipitated were somewhat less at 98°C.

7. Ortho ferric hydroxide formed at 98°C. has smaller adsorptive prop-

erties than a precipitate formed at room temperature. The amounts of nickel, cobalt, or magnesium adsorbed on a precipitate formed at 98°C. were approximately one-half of those adsorbed on a precipitate formed at room temperature.

REFERENCES

- (1) FLECK, H. R., AND WARD, A. M.: *Analyst* **58**, 388 (1933).
- (2) KOLTHOFF, I. M., AND FURMAN, N. H.: *Volumetric Analysis*, Vol. II, p. 479. John Wiley and Sons, Inc., New York (1928).
- (3) KOLTHOFF, I. M., AND GRIFFITH, F. S.: *J. Phys. Chem.* **42**, 541 (1938).
- (4) KOLTHOFF, I. M., AND MOSKOVITZ, B.: *J. Phys. Chem.* **41**, 629 (1937).
- (5) KOLTHOFF, I. M., AND PEARSON, E. A.: *Ind. Eng. Chem., Anal. Ed.* **4**, 147 (1932).
- (6) KOLTHOFF, I. M., AND STENGER, V. A.: *Ind. Eng. Chem., Anal. Ed.* **7**, 79 (1935).
- (7) LANG, R.: *Z. anal. Chem.* **102**, 8 (1935).
- (8) LEVY, L. S.: *Compt. rend.* **189**, 426 (1929).

A DIELECTRIC STUDY OF THE GELATIN-WATER SYSTEM: ANOMALOUS DISPERSION IN BOUND (ORIENTED) WATER

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Solutions of many substances of high molecular weight, such as gelatin, casein, starch, gum arabic, and Congo red, show a rapid increase in electric conductance with increasing frequency (24, 25, 53, 54). Largely independent investigations show that the dielectric constants of some of these and other similar systems increase with decreasing frequency and that values for the dielectric constant many times higher than that of the solvent may be obtained at low frequencies (7, 8, 10, 16, 25, 27, 28, 29, 31, 36, 39, 40, 44, 47, 50, 51, 63). Observers of the dispersion in electric conductance have usually interpreted their results by assuming that the electrolytic ions of the solvent are bound electrostatically to the charged molecules of the dissolved substance, i.e., the dispersion is supposed to be of the same origin as that found in strong electrolytes and treated theoretically by Debye and Falkenhagen (18). On the other hand, observers of the dielectric constant have tended toward picturing the molecules of the dissolved substances as dipoles oriented by the external field. It becomes clear, however, when the complete experimental material is considered, that these two mechanisms cannot account fully for the dielectric behavior of these systems or even be the essential factors in some of the cases. This has been recognized in some of the more recent work in this field (10, 25, 27, 36, 48). It appears in these systems that we are dealing with the same type of interphasial process that, in a more dominant way, influences the dielectric behavior of more coarsely dispersed systems (suspensions, colloids; for literature, see reference 25). The purpose of this work is to produce support for this view by a more extended study of the dielectric properties of the gelatin-water system. Although the nature of this interphasial process is still uncertain, we believe it probable that the underlying mechanism is an abnormal polarizability of the multimolecular film of oriented water molecules at the interphase. This conception will be discussed in some detail below.

The probable bearing of this interphasial dielectric mechanism on the

dielectric behavior of systems of wide practical importance is worth remarking upon, for the same type of phenomenon is observed in living cells, soils, and various kinds of commercially used hygroscopic insulators (paper, fabrics).

EXPERIMENTAL PROCEDURE

The dielectric constants and electric conductances of the gelatin-water systems were measured in alternating fields at frequencies from 0.002 to 65.6 megacycles. The procedure has been described in recent papers (25, 26). The electrolytic cell containing the unknown solution is balanced against a similar cell containing a potassium chloride solution. At frequencies over 2 megacycles the condition of equivalence is established by comparing the cells in a resonance circuit, while a bridge is used for this purpose at the lower frequencies. Equivalence is obtained by varying the concentration of potassium chloride and a parallel condenser. At frequencies over 2 megacycles the chief part of the capacity difference between the cells is compensated for on a specially designed microcondenser which is built into the cell mounting. This condenser has no scale for reading its capacity directly, but every time it is reset its value is measured on a low-frequency bridge. This calibration was sometimes omitted, leaving us then only measurements of the electric conductance.

At the highest frequencies the dispersion in conductance of gelatin-water results to an appreciable extent from the dielectric absorption of the solvent. At low concentrations of the protein this factor may be considered to be substantially eliminated by the experimental procedure used, since our measurements give us directly the difference in dispersion between the gelatin solution and the potassium chloride solution. We introduce as before (cf. 26)

$$\kappa_p^d(\omega) = \kappa_{\text{KCl}}(o) - \kappa_p(o)$$

where $\kappa_{\text{KCl}}(o)$ is the low-frequency conductivity of the potassium chloride solution that balances the gelatin at the frequency ω and $\kappa_p(o)$ is the low-frequency conductivity of the gelatin. At the low concentrations of potassium chloride used, the dispersion in conductance of the potassium chloride solution may, with sufficient accuracy, be taken as equal to that of the solvent; consequently the value κ_p^d represents the amount by which the dielectric absorption of the gelatin system exceeds that of the solvent.

At the higher gelatin concentrations it might be considered preferable to give the true values for the conductance dispersion as obtained by correcting κ_p^d for the dispersion of the water. However, at gelatin concentrations over 5 per cent the dispersion of the gelatin solutions is so high compared to the dispersion of water that this differentiation is without practical importance.

Unless otherwise stated, the measurements were carried out at 21.0°C.

EXPERIMENTAL RESULTS

The gelatin systems were prepared by dissolving purified gelatin from the Eastman Kodak Company in the solvent at approximately 50°C.; the solution was placed in the conductivity cell and allowed to cool until temperature equilibrium was reached. The concentration is given in grams of gelatin per 100 cc. The ash content of the gelatin is 0.3 mg. per gram of gelatin. The low-frequency conductivity of the gelatin gels (aged) as a function of the gelatin concentration is shown in figure 1.

Hysteresis

It is well known that the gelatin-water system, when brought from one temperature to another, shows pronounced hysteresis, so that days may elapse after a new temperature has been established before constant proper-

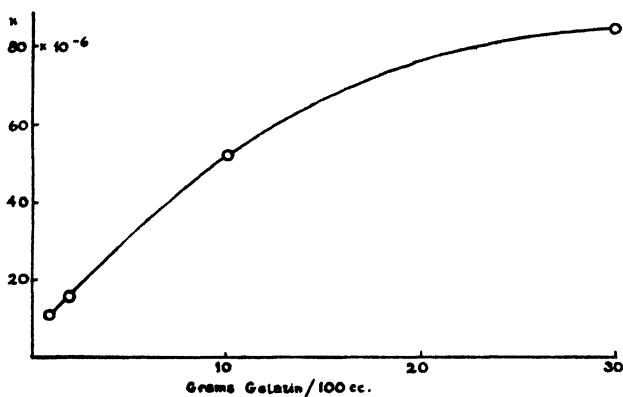


FIG. 1. The low-frequency electrical conductivity of isoelectric gelatin gels of different concentrations.

ties are obtained. The low-frequency conductivity and the dielectric constant are both responsive to this condition, and various types of hysteresis curves based on these two characteristics have already been published (50, 51).

When the gelatin-water system is brought from a higher to a lower temperature, the after effect in both electric conductance and dielectric constant is a decrease which takes place at a continuously decreasing rate, while for a transition from low to high temperature a variation in the opposite direction is obtained. As long as too high temperatures are not used, the observations are perfectly reversible. As is true for other physical characteristics, neither the electric conductance nor the dielectric constant shows any abrupt change at any point during the sol-gel transformation. These results were confirmed in our own work, and it was found that a corresponding behavior is shown by the dielectric absorption. For

systems of different concentrations figure 2 shows the values of κ_p^d (at 65.6 megacycles) that were obtained at different times after these systems were brought from 50°C. to 21.0°C. Even after 4 days the values of κ_p^d are not constant. In fact, when plotted in a logarithmic scale, the values decrease nearly linearly with time during the limited period over which these observations were made.

Variation of frequency

The influence of the frequency of the measuring alternating field on the dielectric characteristics was determined for aged isoelectric gelatin gels of

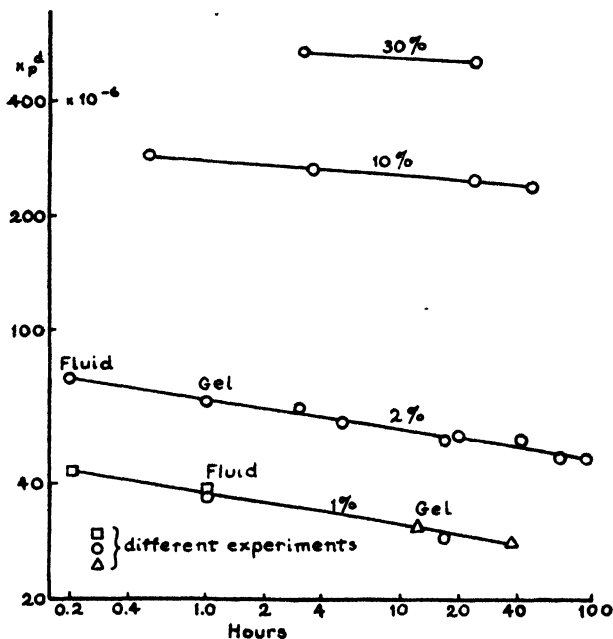


FIG. 2. The effect of aging on the dielectric absorption of isoelectric gelatin. Frequency 65.6 megacycles.

different concentrations up to 46.5 per cent. At the highest concentration ϵ and κ_p^d were measured between 0.002 and 65.6 megacycles, while at lower concentrations measurements were made above 2 megacycles only, and in most cases only κ_p^d was determined. Under the conditions used $\Delta\epsilon$ [that is, $\epsilon(\omega) - \epsilon(2\omega)$] and κ_p^d vary approximately as powers of the frequency.

$$\Delta\epsilon \sim \omega^{-x} \quad (1)$$

$$\kappa_p^d \sim \omega^y \quad (2)$$

The results of measurements on different samples of gelatin show some variation from each other, and while in some experiments expressions 1

and 2 are found to represent the results very satisfactorily, in others the agreement is less perfect. Whether this lack of reproducibility represents actual differences between the different samples of the gelatin or is due to experimental errors is still uncertain.

For the range of gelatin concentrations studied the values of the exponents x and y appear to be independent of the gelatin concentration.

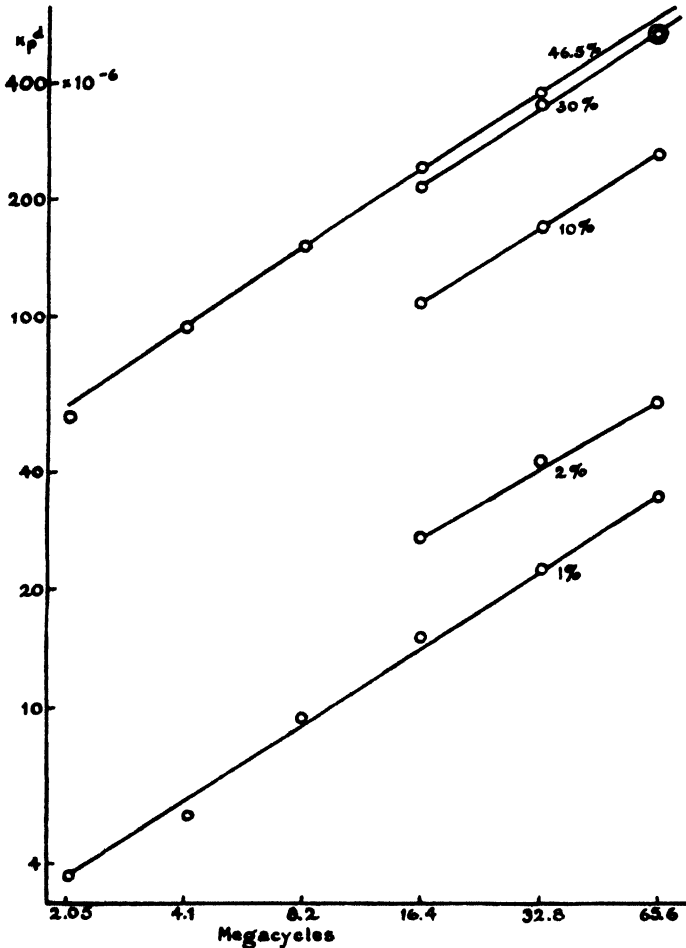


FIG. 3. The dielectric absorption as a function of frequency for isoelectric gelatin gels of different concentrations.

From results on other systems it is probable that the values would show dependence on concentration at concentrations over 50 per cent. The average values of x and y are

$$x = 0.34$$

$$y = 0.66$$

As is to be expected on theoretical grounds (22), the sum of x and y equals unity. Representative frequency curves are shown in figures 3 and 4.

A series of measurements was carried out to determine whether the relation of κ_p^d to frequency changed during the aging of the gelatin system. Isoelectric gelatin systems of different concentrations were kept for several hours at 50°C.; then they were brought to 21.0°C. and at different times

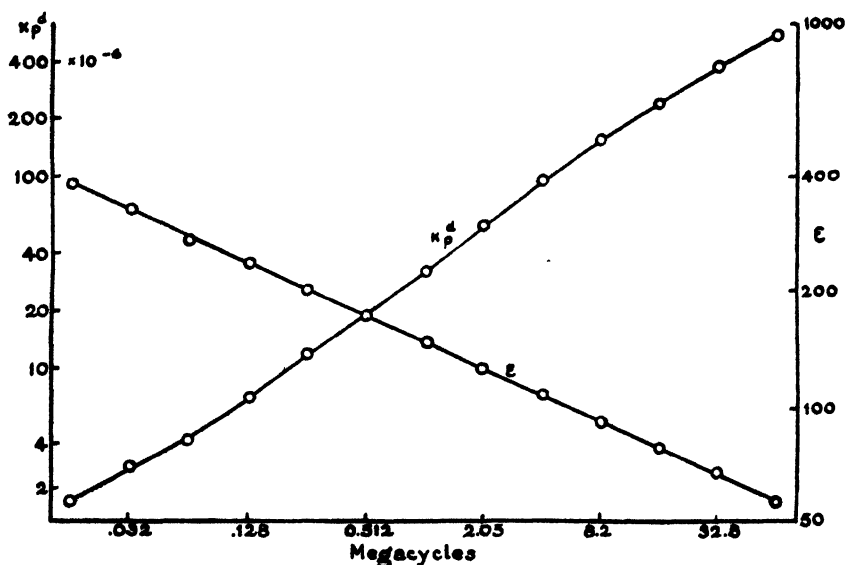


FIG. 4. The dielectric absorption (κ_p^d) and dielectric constant (ϵ) as functions of frequency for 46.5 per cent isoelectric gelatin gel.

thereafter κ_p^d was measured between 16.4 and 65.6 megacycles. The results are shown in figure 5. As far as we can tell from these observations, the relation $\kappa_p^d \sim \omega^y$ remains valid during the aging of the systems and there is no change in the value of the exponent. The observations on the 1 per cent gelatin include the transition sol-gel.

Variation of gelatin concentration

The dependence of κ_p^d on the gelatin concentration is represented in figure 6; the measurements were made at a frequency of 65.6 megacycles. Up to about 5 per cent κ_p^d increases very nearly as the concentration. At

higher concentrations the increase is less rapid, and from about 40 per cent on κ_p^d decreases with increasing concentration.

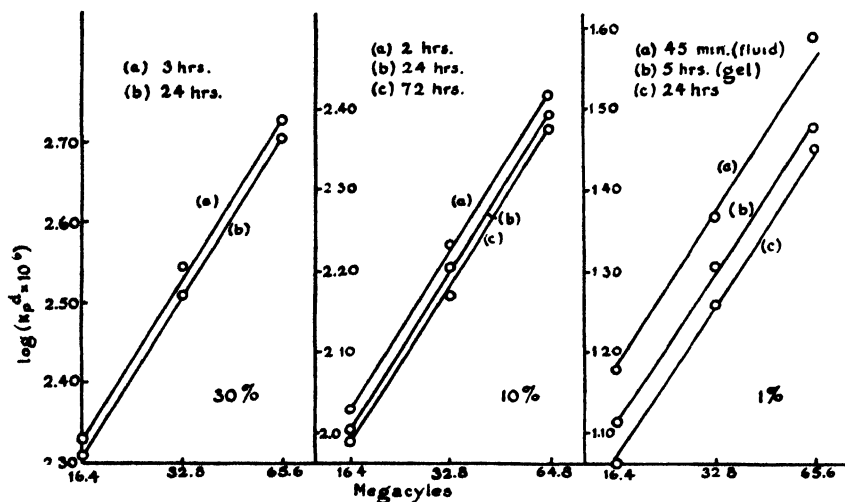


FIG. 5. The effect of aging on the relation of dielectric absorption to frequency for isoelectric gelatin.

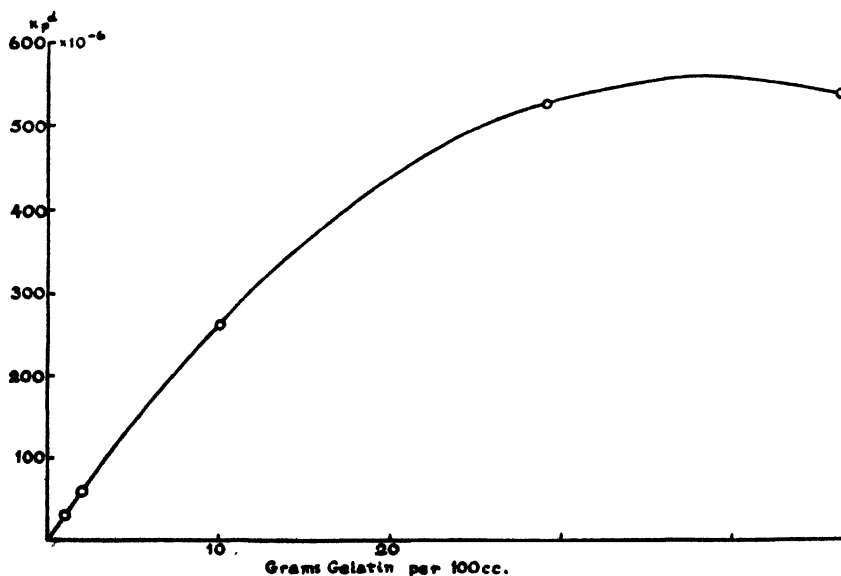


FIG. 6. The dielectric absorption of isoelectric gelatin as a function of its concentration. Frequency 65.6 megacycles.

Addition of hydrochloric acid, sodium hydroxide, and sodium chloride

The effect on κ_p^d of adding 0.002 *M* hydrochloric acid, 0.002 *M* sodium hydroxide, and 0.002 *M* sodium chloride to 1 per cent aged gelatin gels is

represented in figure 7. Measurements were made between 2.05 and 65.6 megacycles. No detectable change is produced in κ_p^d by adding the acid or salt, while the addition of the base causes κ_p^d to increase. Within the range of frequencies studied the results on all these systems may be represented by $\kappa_p^d \sim \omega^\nu$ and the exponent is the same as in the case of the isoelectric gel. The low-frequency dielectric constant shows a similar behavior, in accordance with results already reported by Denekamp and Kruyt (10). These observers extended their measurements over a wider range of pH values, and found that for gelatin gels the dielectric constant is also increased by the addition of acid, although, in accordance with our results, the effect of adding acid was found to be smaller than that of adding base. These authors also tested the effect of adding certain ions

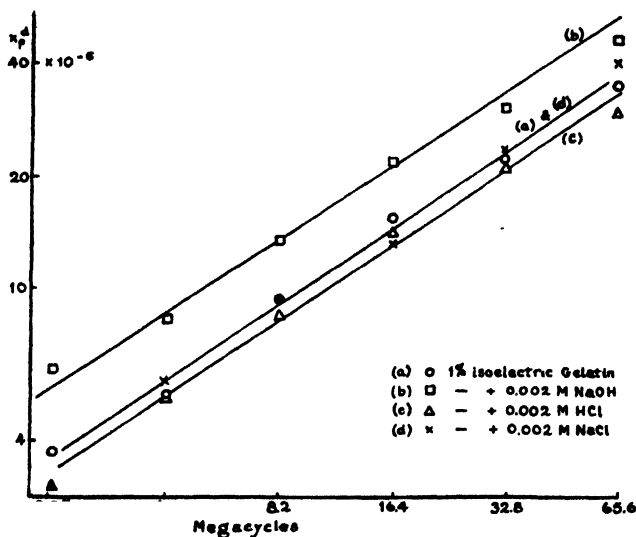


FIG. 7. The dielectric absorption of 1 per cent gelatin gel after adding hydrochloric acid, sodium hydroxide, or sodium chloride.

of high valence, but were unable to detect any change in the dielectric constant.

Denekamp and Kruyt found that gelatin sols behaved differently from the gels as regards the effect of adding acid or base, i.e., the dielectric constant of the sol was decreased by adding acid, and while it was increased by adding base, the increase was much smaller than that obtained for the gels.

Influence of field strength

The intensity of the measuring field was varied between 0.5 and 2 volts per centimeter. Within this range the dielectric characteristics showed no dependence on the field intensity.

DISCUSSION

Since the aged gelatin gels can contain at the most only small quantities of the sol, and since the amount of sol present in a gel may be assumed to decrease rapidly with aging, while the dielectric characteristics decrease comparatively little with aging, the indication is that orientation of the gelatin dipole molecules in the external field plays no appreciable part in the dielectric behavior of aged gelatin gels.

On the other hand, the orientation of molecular dipoles would be expected to play some rôle in the dielectric behavior of gelatin sols. From their observations on the change in the dielectric constant of gelatin sols and gels with pH, Denekamp and Kruyt (10) concluded that the difference in polarizability of the sol and the aged gel (at 1.2 megacycles) represents the influence of the molecular dipoles. Our observations indicate that this is not wholly so. The dielectric mechanism effective in the aged gels appears to be present to an increased extent in the sol, and this accounts for at least an appreciable part of the difference in polarizability between the two states. However, more complete measurements on the frequency dependence of the dielectric characteristics of the sols are required before the influence of the molecular dipoles can be definitely established.¹

Since the gelatin micelles are electrically charged, they bind the ions of the solvent electrostatically. The ions will therefore contribute to the dielectric properties of the gelatin gels in a way similar to that found in the case of strong electrolytes (Debye-Falkenhagen effect). The average number of positive and negative elementary charges on a gelatin molecule at the isoelectric point is probably about ten (33), but the charges are so distributed that the electrostatic forces are comparatively weak. Isoelectric gelatin appears to act approximately as a 2-2 valence type electrolyte (3, 35, 45, 55). At the low electrolyte concentrations with which we have worked, the ions would therefore not be expected to contribute to any appreciable extent to the polarizability of the gelatin systems. This is confirmed by the finding that the addition of sodium chloride or hydrochloric acid to the isoelectric gelatin gels produces no change in ϵ or κ_p^d , although these substances were added in sufficient quantities to increase

¹ Dielectric constant-frequency curves have been determined for solutions of such proteins as carboxyhemoglobin, serum albumin, and serum globulin (1, 16, 47). The curves show anomalous dispersion which was assumed to be of the Debye type. It seems unlikely that these proteins should show no polarizability of the type found in gelatin, although this effect is probably not as great as it is in gelatin. More extended frequency measurements are needed to ascertain the true state of affairs in these systems.

Measurements that we have carried out on egg albumin between 2.0 and 65.6 megacycles show the presence of the interphasial dielectric effect, but to a much smaller degree than in the case of gelatin. When the albumin is denatured by heating, it behaves dielectrically more nearly like gelatin.

the low-frequency conductance by a factor of more than 10. In adding hydrochloric acid, besides changing the ionic strength, we produced an appreciable change in the charges on the gelatin, which should have changed the dielectric characteristics of the gelatin if electrostatically bound ions had played an important rôle.

The same conclusion as to the negligible importance of the electrostatic binding of the ions of the solvent results from the fact that in all cases studied we can account very closely for the observed low-frequency conductivities of the gelatin systems (restricting ourselves to the low gelatin concentrations) on the basis of the ions known to be present in the systems if these are assumed to have the same mobilities as they have in the absence of gelatin. The agreement is so close, compared to the observed high-frequency increase in conductance, as to leave no doubt that this increased conductance cannot be produced by the ions.

In verifying this statement, let us first consider the isoelectric gelatin gels to which no electrolytes were added. The low-frequency conductivity of 1 per cent gelatin is $12 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$ (figure 1). Nearly half of this conductivity is accounted for by the hydrogen ion. The remaining part may be accounted for by electrolytic impurities, the ash content of the gelatin being 0.3 mg. per gram of gelatin. In any case it is clear that the amount of free organic electrolytes in the gelatin must be small, and that the total amount of electrolytes is wholly insufficient to account for the high-frequency conductivity values, which at 65.6 megacycles are over $30 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$ for 1 per cent gelatin and are still increasing rapidly with increasing frequency.

Let us now consider the low-frequency conductivity of gelatin gels to which known amounts of sodium chloride, hydrochloric acid, or sodium hydroxide were added. Adding 0.002 *M* sodium chloride to 1 per cent isoelectric gelatin increases the low-frequency conductivity from 12×10^{-6} to $229 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$; the difference is $217 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$. The conductivity of 0.002 *M* sodium chloride itself (without the gelatin) is $226 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$. The difference is 4 per cent, part of which must be due to the obstruction to the current that the gelatin offers simply by its bulk. The decrease in the conductance of the sodium chloride produced by its electrostatic binding by the gelatin can therefore be but a few per cent at the most, while the high-frequency increase in conductance (of 1 per cent isoelectric gelatin plus 0.002 *M* sodium chloride) is about 15 per cent at 65.6 megacycles.

Similarly, the addition of 0.002 *M* hydrochloric acid to 1 per cent isoelectric gelatin causes an increase in its low-frequency conductivity of $148 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$. The change in pH is from 4.9 to 4.3, corresponding to a change in the conductivity of the hydrogen ions of $12 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$. The conductivity of 0.002 *M* chloride ion is 139×10^{-6}

$\text{ohm}^{-1} \text{ cm.}^{-1}$, assuming negligible electrostatic forces. The sum of these two conductivities is $151 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$, agreeing to within 2 per cent with the observed change in low-frequency conductivity of the gelatin.

Finally, the addition of 0.002 *M* sodium hydroxide to 1 per cent iso-electric gelatin causes an increase in the low-frequency conductivity of $89 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$. The change in pH is from 4.9 to 5.8, corresponding to a decrease in the conductivity of the hydrogen ions of $3 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$. The conductivity of 0.002 *M* sodium ion is $93 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$. The difference between these two conductivities agrees to within 1 per cent with the observed increase in the conductivity of the gelatin.

To reach an understanding of the dielectric behavior of gelatin, let us consider the dielectric properties of more coarsely dispersed systems (25).

If we suspend a small quantity of any finely divided dielectric (as, for example, glass) in water, a striking change in dielectric properties results. The system shows strong anomalous dispersion accompanied by high energy absorption. Dielectric constant values as high as 100,000 may be obtained at very low frequencies. An interesting feature of this phenomenon is the form of the frequency dependence. For most of the many different systems studied $\Delta\epsilon/\Delta\omega$ and $\Delta\kappa/\Delta\omega$ vary as powers of the frequency over the wide range of frequencies studied (0.5 to 2000 kilocycles), and in all cases this law represents the observations with a considerable degree of approximation. Other results, about whose generality, however, we are not very well informed, are as follows: The values of $\Delta\epsilon/\Delta\omega$ and $\Delta\kappa/\Delta\omega$ increase with increasing temperature and with increasing electrification of the interphase, and are independent of the presence of moderate concentrations of sodium chloride or potassium chloride in the suspending medium. A study of the influence of the size of the suspended particles showed that, for constant volume of the suspended material, $\Delta\epsilon/\Delta\omega$ and $\Delta\kappa/\Delta\omega$ increase as the internal surface, for particle sizes down to about 1μ in diameter. From this result it was concluded that the origin of these singular dielectric properties is a polarization of the region at or near the interphase, by the external field, in the direction parallel to the interphase.

It has been known for a long time that the dielectric constant of many colloids is much higher than that of water (13, 14, 24, 25, 27, 28, 30, 32, 44). One of the best known systems is that of colloidal vanadium pentoxide, first investigated by Errera (13, 14). This author believed that the reason for the high dielectric constant was an orientation of the colloidal dipole particles in the external field. Later work made it clear that this cannot be the correct explanation (24, 25, 27, 28, 32).

There seems no reason to doubt that the dielectric peculiarities shown by systems of colloidal dispersion are chiefly of the same origin as those observed in suspensions. The high dielectric constant of many

colloids is quite consistent with what we should expect from the observations on suspensions if the polarizability were determined essentially by the internal surface independent of particle size. On the other hand, very highly dispersed colloids generally show dielectric characteristics comparatively little different from those of water, so it is evident that the polarizability does not keep on increasing with the internal surface when the particle size becomes very small, but that high polarizability is a property of comparatively large interphases only. That this must be so is of course clear, since systems of molecular dispersion show none, or only traces, of these interphasial dielectric characteristics. The polarizability appears to decrease with decreasing particle size below, say, diameters of 100 or 1000Å.

The knowledge that we now have of the dielectric behavior of gelatin gels leaves little doubt that the singular dielectric properties of these systems originate in this same type of interphasial process. The influence of frequency, temperature, electrification of the micelles, and added salts is similar to that found in suspensions. Even though the exact significance of these different results is somewhat uncertain, taken together they seem sufficient to show that we are dealing with the same phenomenon.

Since all interphases examined so far show this characteristic high polarizability, we must clearly look for an explanation of a very general character. A likely possibility is that the polarizability is a property of the layer of comparatively highly oriented water molecules which, there are good reasons to believe, is present at all interphases (2, 4, 5, 11, 12, 20, 38, 60). (This water is to be more or less closely identified with "adsorbed" or "bound" water.) In various mechanical characteristics this layer appears to behave more like a solid than a fluid, and so it does not seem unreasonable to assume that under the influence of an electric field the layer would show polarizability properties approximating those of many dipolar crystalline solids, i.e., it is less polarizable than normal water at very high frequencies, but it becomes more highly polarizable than water when the frequency is low.

It may be questioned whether an increased orientation of the water molecules alone would be sufficient to produce such marked changes in polarizability as we observe at interphases. To this the reply should be made, first, that it is possible that the changed properties of the water near interphases may lie in more than an increased orientation, i.e., there may be an actual change in molecular pattern. For the present, however, the weight of the evidence seems to be against such a conception. Furthermore, it should be recognized that the high electric moment of the water molecule gives water a tendency toward self-polarization, so that a comparatively small change in molecular arrangement may produce a marked change in its polarizability. The remarkable "ferromagnetic" dielectric

properties of certain crystals (Rochelle salts, magnesium platinocyanide, and yttrium platinocyanide) containing large amounts of crystal water may be remarked upon in this connection, for these properties appear to originate in the loosely bound water and, within certain ranges of temperature and frequency, are very similar to those found at interphases (6, 17, 62). The observations of Smyth (57) on the marked increase in the low-frequency dielectric constant of ice resulting from the presence of small quantities of such salts as potassium chloride in the ice are also interesting.

The situation in the water near the interphase may in certain respects be similar to that found in dipole solids near their melting points or near temperatures at which changes from one molecular arrangement to another take place. Around these transition points marked increases in dielectric constant and dielectric absorption are often observed (15, 49, 52, 57).

Inside regions of anomalous dispersion the dielectric constant and dielectric absorption of dipole systems generally increase with increasing temperature, reflecting, according to Debye, an influence of the viscosity on the orientation of the dipoles in the external field. This law generally holds for dipolar solids also. The result that the interphasial dielectric characteristics increase with increasing temperature is therefore consistent with our conception of their origin, although the influence of the temperature, by its effect on the viscosity, presumably would be masked in part by a direct influence of the temperature on the structure of the interphasial water.

The fact that the interphases lose their high polarizability when the suspended particles are very small is explained partly because the depth of the interphasial water film decreases at high dispersions and partly because the high polarizability of the interphasial water would be assumed to result from a "coöperative" behavior of the water molecules, which would require a certain extension of the interphase to be effective.

If our theory of the interphasial polarizability is correct, then we should be able to obtain confirmatory evidence by experimenting with dispersed systems containing such small quantities of water that the interphasial water films cannot be developed fully. Consider the observations on gelatin gels shown in figure 6. The dielectric absorption reaches its highest value at a gelatin concentration of 40 per cent. The reason may be that the internal surface of the gelatin gels decreases with increasing concentration at concentrations over this value. However, the presence of the maximum may also be interpreted as meaning that at the concentration at which it occurs all the water is "bound," in the sense of its dielectric characteristics. This gives a value for the "bound" water of 1.5 g. of water per gram of gelatin. This value is three or four times higher than the generally accepted value for the hydration, but it is quite consistent with the values for bound water obtained by the various other methods that have been used to differentiate between free and bound water in gelatin (34, 37, 41, 46, 58, 59).

In a previous paper (25) we showed curves representing the dielectric constant of suspensions of finely powdered dielectric materials (Pyrex glass, kaolin) as a function of their volume concentration. The curve for Pyrex glass shows a maximum at a concentration of 26 per cent. The curves for kaolin were not brought to sufficiently high concentrations to reach a maximum, but the part of the curves obtained indicates that a maximum will be reached at a concentration not greatly different from that for Pyrex glass. These measurements were carried out at a frequency of 2 kilocycles and the average particle size appeared, by microscopic examination, to be around 0.5 to 1 μ in diameter, although it may possibly have been very much smaller. At the time these observations were made it was assumed that this decrease in the dielectric constant at high concentrations resulted from a decrease in internal surface, because of aggregation. On the basis of our present conception the decrease may be interpreted as resulting from an "overlapping" of the interphasial water films of the different particles. If this is the correct explanation, we should expect the relation of dielectric constant to frequency to change when the volume concentration is high. This has been found to be the case. In the concentrated suspensions the dielectric constant decreases less rapidly with increasing frequency than in suspensions of low concentration. Or, expressed in another way, the curve representing the dielectric constant as a function of concentration reaches its maximum at a volume concentration which is lower as the frequency is lower. If we accept the interpretation given, it would appear that the depth of the interphasial water film must be of the order of 1000 Å. This is a very high value, though abnormalities in various physical characteristics of thin water films have been observed to set in at thicknesses of this order of magnitude (2, 5, 11, 12, 20, 38, 60).

Observations of interest in this connection are also found in the literature dealing with the influence of humidity on the dielectric properties of fibrous or gel-like insulating substances such as Bakelite, paper, fabrics, or rubber. The consideration of these data must, however, be reserved for another place.

In conclusion, it should be remarked that the interphasial dielectric phenomena dealt with in this paper probably play an essential rôle in the dielectric behavior of a number of important systems. (1) It has been known for a long time that the dielectric constant and dielectric absorption of living cells are very high at low frequencies and that these high values originate in the water-permeable gel-like membranes that surround the cells (9, 21, 23). (2) Because of their importance in radio communication, the dielectric properties of soils have been studied extensively during recent years over wide ranges of frequency. Very high dielectric constant values were observed at low frequencies, and marked increases in electric

conductance were obtained at very high frequencies (19, 56). (3) It is well known that the dielectric properties of many commercially used dielectrics of a gel-like or fibrous structure, such as Bakelite, paper, and fabrics, are influenced by their water content to an extent wholly unexplainable by any mixture law if the adsorbed water had anything like its usual dielectric properties (42, 43, 61). (4) Metal electrodes in inactive solutions (such as nickel in sodium chloride) act dielectrically as if a capacity and a series resistance were interposed between the metal and the solution. The capacity and the resistance both vary as powers of the frequency (22). This behavior may be accounted for by the presence of thin, poorly conducting, surface films (metal oxides) containing a considerable quantity of adsorbed water.

SUMMARY

At frequencies between 0.002 and 65.6 megacycles and for field intensities between 0.5 and 5 volts per centimeter the dielectric constant and dielectric absorption of gelatin-water systems were determined under different conditions of gelatin concentration, pH, ionic strength, and structural state. The results indicate that the dielectric properties of these systems are dependent on a polarization at the interphases similar to that already known to be present in more coarsely dispersed systems. It is suggested that this polarization originates in the interphasial layer of oriented water molecules, and various types of evidence in support of this hypothesis are discussed. The bearing of this on the dielectric behavior of hygroscopic insulators (paper, fabrics), soil, cell membranes, and metal electrodes is pointed out.

REFERENCES

- (1) ARRHENIUS: *Physik. Z.* **39**, 559 (1938).
- (2) BANGHAM, MOSALLAIN, AND SAWERIS: *Nature* **140**, 237 (1937).
- (3) BIGWOOD: *Trans. Faraday Soc.* **31**, 335 (1935).
- (4) BRESLER AND POCHIL: *Acta Physicochim. (U.R.S.S.)* **8**, 129 (1938).
- (5) BULL AND WRONSKI: *J. Phys. Chem.* **41**, 463 (1937).
- (6) BUSCH: *Helv. Phys. Acta* **11**, 269 (1938).
- (7) CAVALLARO: *Boll. soc. ital. biol. sper.* **9**, 925 (1934).
- (8) CAVALLARO: *Arch. sci. biol.* **20**, 572 (1934).
- (9) COLE: *Cold Spring Harbor Symposia Quant. Biol.* **1**, 107 (1933).
- (10) DENEKAMP AND KRUYT: *Kolloid-Z.* **81**, 62 (1937).
- (11) DERJAGUIN: *Z. Physik* **84**, 657 (1933).
- (12) DERJAGUIN: *Acta Physicochim. (U.R.S.S.)* **5**, 1 (1936).
- (13) ERRERA: *Kolloid-Z.* **31**, 58 (1922); **32**, 157, 240, 373 (1923).
- (14) ERRERA: *J. phys. radium* **4**, 225 (1923); **5**, 304 (1924).
- (15) ERRERA: *Trans. Faraday Soc.* **24**, 162 (1928).
- (16) ERRERA: *J. Chem. Phys.* **29**, 577 (1932).
- (17) ERRERA AND SACK: *Trans. Faraday Soc.* **30**, 687 (1934).
- (18) FALKENHAGEN: *Elektrolyte. S. Hirzel, Leipzig* (1932).
- (19) FELDMAN: *Proc. Inst. Radio Engrs.* **31**, 764 (1933).

- (20) FRAZER, PATRICK, AND SMITH: *J. Phys. Chem.* **31**, 897 (1927).
- (21) FRICKE, H.: *Physics* **1**, 106 (1931).
- (22) FRICKE, H.: *Phil. Mag.* **14**, 310 (1932).
- (23) FRICKE, H.: *Cold Spring Harbor Symposia Quant. Biol.* **1**, 117 (1933).
- (24) FRICKE, H., AND CURTIS: *Phys. Rev.* **48**, 775 (1935).
- (25) FRICKE, H., AND CURTIS: *J. Phys. Chem.* **41**, 729 (1937).
- (26) FRICKE, H., AND PARTS: *J. Phys. Chem.* **42**, 1171 (1938).
- (27) FRICKE, R.: *Kolloid-Z.* **56**, 166 (1931).
- (28) FRICKE, R., AND HAVESTADT: *Z. anorg. Chem.* **196**, 120 (1931).
- (29) FÜRTH: *Ann. Physik* **70**, 64 (1923).
- (30) FÜRTH AND BLÜH: *Kolloid-Z.* **34**, 259 (1924).
- (31) HALLER: *Kolloid-Z.* **56**, 170 (1931).
- (32) HAVESTADT AND FRICKE, R.: *Z. anorg. Chem.* **188**, 357 (1930).
- (33) HITCHCOCK: *J. Gen. Physiol.* **15**, 125 (1931).
- (34) JONES AND GORTNER: *J. Phys. Chem.* **36**, 387 (1932).
- (35) JOSEPH: *J. Biol. Chem.* **116**, 353 (1936).
- (36) KRUYT AND OVERBEEK: *Kolloid-Z.* **81**, 257 (1937).
- (37) LLOYD AND MORAN: *Nature* **132**, 515 (1933).
- (38) MCHAFFIE AND LENHER: *J. Chem. Soc.* **127**, 1559 (1925).
- (39) MARINESCO AND GIRARD: *Compt. rend. soc. biol.* **102**, 726 (1929).
- (40) MAY AND SCHAEFFER: *Z. Physik* **73**, 452 (1931).
- (41) MORAN: *Kolloid-Z.* **59**, 217 (1932).
- (42) MURPHY AND WALKER: *J. Phys. Chem.* **33**, 200 (1929).
- (43) MURPHY AND LOWRY: *J. Phys. Chem.* **34**, 598 (1930).
- (44) NANTY AND VALET: *Compt. rend.* **194**, 883 (1932).
- (45) NORTROP AND KUNITZ: *J. Gen. Physiol.* **11**, 477 (1928).
- (46) NORTROP AND KUNITZ: *J. Phys. Chem.* **35**, 162 (1931).
- (47) ONCLEY AND FERRY: *J. Am. Chem. Soc.* **60**, 1115, 1123 (1938).
- (48) PIEKARA: *Kolloid-Z.* **52**, 179 (1930); **58**, 283 (1932); **59**, 12 (1932).
- (49) PIEKARA: *Physik. Z.* **31**, 579 (1930).
- (50) PIEKARA: *Compt. rend.* **198**, 803 (1934).
- (51) PIEKARA: *Kolloid-Z.* **73**, 273 (1935).
- (52) PIEKARA: *Physik. Z.* **37**, 624 (1936).
- (53) SCHAEFER: *Physik. Z.* **77**, 117 (1932).
- (54) SCHMID ET AL.: *Z. Elektrochem.* **42**, 727, 781 (1936); **43**, 907 (1937).
- (55) SIMMS: *J. Gen. Physiol.* **11**, 613 (1928).
- (56) SMITH-ROSE: *J. Inst. Elec. Engrs. (London)* **75**, 221 (1934).
- (57) SMYTH: *Chem. Rev.* **19**, 329 (1936).
- (58) SØRENSEN: *Z. physiol. Chem.* **103**, 15 (1918); **106**, 1 (1919).
- (59) SVEDBERG: *J. Am. Chem. Soc.* **46**, 2672 (1924).
- (60) TALMUD ET AL.: *Z. physik. Chem.* **A151**, 401 (1939); **A154**, 277 (1931).
- (61) YAGER AND MORGAN: *J. Phys. Chem.* **35**, 2026 (1931).
- (62) ZELENY AND VALASEK: *Phys. Rev.* **46**, 450 (1934).
- (63) ZHILENKOV: *Colloid J. (U.S.S.R.)* **1**, 223 (1935).

SPECIFIC THERMODYNAMIC PROPERTIES OF DILUTE IONIC SOLUTIONS

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The thermodynamic properties of ions in extremely dilute aqueous solutions of strong electrolytes are quantitatively described by the well-known interionic attraction theory of Debye and Hückel (3). Individual deviations from this limiting law occur at ionic strengths, say, about 10^{-3} to 10^{-2} molal. Most of these may be accounted for by taking into consideration the different ionic diameters, due to the size of the ions, and the different degrees of hydration (8).

At these low concentrations mixtures have frequently been treated according to the Lewis and Randall (12) "principle of ionic strength", which states that the activity coefficient of an electrolyte is constant at constant total ionic strength. At ionic strengths about 10^{-1} , however, the individual specific properties of electrolytes become more important, and in these solutions the Lewis and Randall principle consequently loses its validity.

We know that these specific properties of ions must depend upon their sizes, electron configuration, polarizabilities, etc., but the theoretical treatment of the problem is not yet definitely solved. In technical calculations, however, it will serve our purpose to take advantage of the empirical fact that at concentrations up to about 10^{-1} molal, the deviations from the Debye-Hückel theory are roughly proportional to the concentration.

SINGLE ELECTROLYTES

For a single electrolyte in water we may then use the following formulas for the activity coefficient γ_{\pm} and the Lewis and Randall function j (for systematics and notation of thermodynamics, see reference 13):

$$-\log \gamma_{\pm} = (-\log \gamma_{\pm})^0 - \nu \lambda m \quad (1)$$

$$j = 1 - \phi = j^0 - 1.15 \nu \lambda m \quad (2)$$

The standard values (the first term on the right-hand side) are given by the following Debye-Hückel relations:

$$(-\log \gamma_{\pm})^0 = \frac{\nu}{2} \left(\frac{z_+^2}{z_+} + \frac{z_-^2}{z_-} \right) \mu^{1/2} / (1 + \mu^{1/2})$$

TABLE 1
Standard values of $-\log \gamma_{\pm}$ and of j^*

IONIC STRENGTH $\frac{1}{2}\sum m_i z_i^2$	$j^0/z_+ z_- $				$(-\log \gamma_{\pm})^0/z_+ z_- $			
	0	25	50	100	0	25	50	100
0.01	0.0323	0.0336	0.0352	0.0378	0.0442	0.0460	0.0482	0.0517
0.02	0.0433	0.0450	0.0472	0.0506	0.0600	0.0624	0.0655	0.0701
0.03	0.0509	0.0529	0.0555	0.0595	0.0717	0.0746	0.0782	0.0838
0.04	0.0568	0.0591	0.0620	0.0664	0.0810	0.0842	0.0884	0.0947
0.05	0.0617	0.0642	0.0673	0.0721	0.0887	0.0922	0.0967	0.1037
0.06	0.0657	0.0683	0.0717	0.0768	0.0955	0.0993	0.1041	0.1116
0.07	0.0693	0.0721	0.0756	0.0810	0.1015	0.1055	0.1107	0.1187
0.08	0.0725	0.0754	0.0791	0.0848	0.1070	0.1113	0.1167	0.1251
0.09	0.0753	0.0783	0.0822	0.0880	0.1122	0.1167	0.1224	0.1312
0.10	0.0781	0.0812	0.0850	0.0911	0.1168	0.1215	0.1275	0.1365
0.11	0.0802	0.0834	0.0875	0.0938	0.1210	0.1258	0.1320	0.1414
0.12	0.0824	0.0857	0.0899	0.0963	0.1250	0.1300	0.1364	0.1461
0.13	0.0844	0.0878	0.0921	0.0987	0.1286	0.1337	0.1403	0.1503
0.14	0.0862	0.0896	0.0940	0.1008	0.1322	0.1375	0.1442	0.1545
0.15	0.0880	0.0915	0.0960	0.1027	0.1357	0.1411	0.1481	0.1586
0.16	0.0894	0.0930	0.0975	0.1045	0.1388	0.1444	0.1514	0.1623
0.17	0.0909	0.0945	0.0992	0.1062	0.1419	0.1476	0.1548	0.1659
0.18	0.0924	0.0961	0.1008	0.1080	0.1448	0.1506	0.1580	0.1693
0.19	0.0938	0.0976	0.1023	0.1096	0.1475	0.1534	0.1609	0.1724
0.20	0.0952	0.0990	0.1039	0.1113	0.1502	0.1562	0.1639	0.1756
0.25	0.1002	0.1042	0.1094	0.1171	0.1620	0.1685	0.1767	0.1894

* The fourth decimal place is only approximate.

TABLE 2
Values of ν for different valence types

VALENCE TYPE	ν
1-1	1
1-2	4/3
1-3	3/2
1-4	8/5
2-2	1
2-3	12/5

and

$$j^0 = 0.7677hz_+|z_-|\mu^{1/2}\sigma(\mu^{1/2})$$

(for convenience $g \times a$ has been set equal to 1, which corresponds to a mean ionic diameter of 3 Å.; any deviation from this diameter will be

TABLE 3
Interaction coefficients

ELECTROLYTE	0°C.	25°C.	ELECTROLYTE	0°C.	25°C.
LiOH.....	-0.07 _s	-0.07	LiClO ₃	+0.22	+0.25
NaOH.....	+0.07	+0.09	LiClO ₄	+0.28	+0.32
KOH.....	+0.12	+0.14	NaClO ₃	+0.02	+0.10
RbOH.....	+0.15	+0.17	NaClO ₄	+0.05	+0.15
CsOH.....	+0.19	+0.21	NaBrO ₃	+0.03	+0.11
LiF.....	-0.5	-0.5	NaIO ₃	-0.36	-0.26
NaF.....	-0.05	-0.03	KClO ₃	-0.18	-0.03
KF.....	+0.3	+0.4	KClO ₄	-0.42	-0.25
NH ₄ F.....	+0.3?		KBrO ₃	-0.21	-0.12
RbF.....	+0.4	+0.45	KIO ₃	-0.37	-0.2
CsF.....	+0.5	+0.55			
LiCl.....	+0.17 _s	+0.19	HCl.....	+0.21	+0.215
NaCl.....	+0.10	+0.13	HBr.....	+0.23	+0.26
KCl.....	+0.03	+0.06	HI.....	+0.23	+0.25
NH ₄ Cl.....	+0.00	+0.03	HClO ₄	+0.22	+0.25
RbCl.....	-0.01	+0.03	HNO ₃	+0.15	+0.19
CsCl.....	-0.10	-0.07			
LiBr.....	+0.25	+0.26	MgCl ₂	+1.2	+1.3
NaBr.....	+0.17	+0.20	MgBr ₂	+1.6	+1.7
KBr.....	+0.06	+0.09	CaCl ₂	+0.8	+0.9
NH ₄ Br.....	+0.01	+0.04	SrCl ₂	+0.55	+0.7
RbBr.....	+0.00	+0.03	BaCl ₂	+0.45	+0.55
CsBr.....	-0.07	-0.03	BaBr ₂	+0.9	+1.0
			BaI ₂	+2.0	+2.1
LiI.....	+0.38	+0.40	ZnCl ₂ , CoCl ₂	+1	+1
NaI.....	+0.30	+0.34	MnCl ₂	+0.7	+0.8
KI.....	+0.13	+0.17	NiCl ₂	+1.1	+1.2
NH ₄ I.....	+0.05	+0.09	FeCl ₂	+1.2	+1.3
RbI.....	+0.00	+0.04	CuCl ₂	+0.6	+0.7
CsI.....	-0.04	+0.00	CuBr ₂	+1.6	+1.7
LiNO ₃	+0.20	+0.22			
NaNO ₃	-0.02	+0.03	Mg(NO ₃) ₂	+0.3	+0.4
KNO ₃	-0.22	-0.17	Ca(NO ₃) ₂	0.0	+0.2
NH ₄ NO ₃	-0.22	-0.17	Sr(NO ₃) ₂	-0.25	0.0
RbNO ₃	-0.23	-0.18	Ba(NO ₃) ₂	-0.4	-0.1
CsNO ₃	-0.28	-0.21	Zn(NO ₃) ₂	+1.0	+1.1
			Ni(NO ₃) ₂	+1.1	+1.2
Li formate.....	+0.10	+0.11	Li ₂ SO ₄	+1.0	+1.1
Na formate.....	+0.13	+0.14	Na ₂ SO ₄	+0.05	+0.2
K formate.....	+0.14	+0.15	K ₂ SO ₄	-0.1	+0.1
Li acetate.....	+0.15	+0.16	Rb ₂ SO ₄	-0.2	0.0
Na acetate.....	+0.22	+0.23	Cs ₂ SO ₄	-0.3	-0.1
K acetate.....	+0.23	+0.24			
Rb acetate.....	+0.23	+0.24	AgNO ₃	-0.21	-0.02
Cs acetate.....	+0.23	+0.25	AgClO ₃	-0.1	+0.1
			TlNO ₃	-0.55	-0.4
			TlCl.....	-0.8	-0.7
			TlClO ₄	-0.4	-0.2
			Tl acetate.....	-0.2	-0.06

TABLE 3—*Concluded*

ELECTROLYTE	0°C.	25°C.	ELECTROLYTE	0°C.	25°C.
LiC ₇ H ₇ SO ₃	+0.1	+0.14	Ba(OH) ₂	-0.07	+0.02
NaC ₇ H ₇ SO ₃	-0.1	0.0	La(NO ₃) ₃	+2.0	
KC ₇ H ₇ SO ₃	-0.3	-0.14	LaCl ₃	+1.5	+1.7
KCNS.....	+0.02	+0.05	La ₂ (SO ₄) ₃	0.0	
KCN.....	-0.05	0.0	K ₃ Fe(CN) ₆	+1.3	+1.5
KMnO ₄	-0.35	-0.2	K ₄ Fe(CN) ₆	+1.3	+1.5

taken account of in the term proportional to m). The coefficient ν is related to the number, ν_+ , of cations and to the number, ν_- , of anions into which the electrolyte dissociated; the relation is given by

$$\nu = 2/(1/\nu_+ + 1/\nu_-)$$

and in table 2 are shown figures for electrolytes of different valence types. The standard values divided by the product of the valences are given in table 1 for different temperatures and ionic strengths.

The coefficient λ is termed the "interaction coefficient" (5). In order to present the available experimental thermodynamic data in a simple and compact form for ready reference, we have calculated the interaction coefficient for some one hundred electrolytes (for sources of data see reference 10). The results are shown in table 3.

MIXTURES

The same interaction coefficients may also be used in the estimation of thermodynamic properties for mixtures of electrolytes. Thus Guggenheim (5) has worked out a convenient method, based on Brönsted's (2) theory of "specific ionic interaction". The formula for the mean practical stoichiometric activity coefficient may thus be written:

$$-\log \gamma_{\pm, x} = (-\log \gamma_{\pm, x})^0 - \frac{\nu_+}{\nu} \sum_{x'} \lambda_{\pm, x'} \times m_{x'} - \frac{\nu_-}{\nu} \sum_{x'} \lambda_{x', \pm} \times m_{x'} \quad (3)$$

The values of $(-\log \gamma_{\pm, x})^0$ at total ionic strength μ are to be taken from table 1, and interaction coefficients, λ , from table 3.

As an illustration we may calculate the activity coefficient of lanthanum chloride in a mixture with hydrochloric acid and potassium nitrate. Equation 3 gives:

$$-\log \gamma_{La, Cl} = [-\log \gamma_{1-3 type}]^0 - \frac{1}{2} \times [\lambda_{La, Cl} \times m_{Cl^-} + \lambda_{La, NO_3} \times m_{NO_3^-}] \\ - \frac{1}{2} \times [\lambda_{H, Cl} \times m_{H^+} + \lambda_{La, Cl} \times m_{La^{+++}} + \lambda_{K, Cl} \times m_{K^+}] \quad (4)$$

The results at 25°C. for different mixtures at constant total ionic strength equal to 0.1 are given in table 4.

Using such equations one may readily obtain the interaction coefficient for an electrolyte from measurements of thermodynamic properties of any other component in a mixture where the first-named electrolyte is present. This may be of great importance in some cases; for example, where suitable electrodes for electromotive force measurements are not available.

TABLE 4
Activity coefficients at constant ionic strength

ELECTROLYTE	γ_{\pm} FOR LaCl_3
LaCl_3 , only	0.445
HCl mainly.	0.463
KNO_3 , mainly	0.495
0.01 <i>m</i> LaCl_3 + 0.02 <i>m</i> HCl + 0.02 <i>m</i> KNO_3	0.458

TABLE 5
Interaction coefficients

ELECTROLYTE	0°C.	25°C.	50°C.
LiOH.	-0.07 ₆	-0.07	-0.06
NaOH	+0.08	+0.09	+0.10
KOH	+0.12	+0.14	+0.16

INDIRECT METHOD

In order to demonstrate the method, we shall compute the interaction coefficient for some alkali hydroxides from the activity coefficient product, $\gamma_{\text{H}^+} \times \gamma_{\text{OH}^-}$, of water in solutions of alkali chlorides and bromides at 0.1 *m*. Omitting the quite negligible terms containing m_{H^+} and m_{OH^-} , equation 3 gives (at 0.1 *m* concentration):

$$-\log \gamma_{\text{H,OH}} = (-\log \gamma_{1-1 \text{ type}})^0 - 0.05(\lambda_{\text{H,Hal}} + \lambda_{\text{Alk,OH}}) \quad (5)$$

From the measurements of $\gamma_{\text{H}^+} \gamma_{\text{OH}^-} / a_{\text{H}_2\text{O}}$ by Harned and Cook (7), we then obtain the interaction coefficients given in table 5 (with $\lambda_{\text{H,Cl}}$ equal to 0.210 (0°C.), 0.215 (25°C.), and 0.22 (50°C.)). From the chloride and bromide series we also found the difference $\lambda_{\text{H,Br}} - \lambda_{\text{H,Cl}}$ at different temperatures, corresponding to the following interaction coefficients for hydrobromic acid: 0.265 (0°C.), 0.28 (25°C.), and 0.29₆ (50°C.).

ACTIVITY OF INDIVIDUAL IONS

It has been pointed out (16) that the concept of individual ionic activity coefficients is without any thermodynamic significance, a supplementary

definition of non-thermodynamic nature being needed. In the concentration range about $\mu = 0.1 m$ and less, Guggenheim (5, 6) has suggested a useful and very simple convention for defining individual ionic coefficients in mixtures and single electrolytes. We may write

$$-\log \gamma_i = (-\log \gamma_{i-i \text{ type}})^0 - \sum_k \lambda_{i,k} \times m_k \quad (6)$$

where the summation \sum_k extends over all ionic species k of opposite sign to that of the species i . $\lambda_{i,k}$ is to be taken from our table 3.

TEMPERATURE EFFECT

The relative partial molal heat content of the solute, $\bar{L}_2 = \bar{H}_2 - \bar{H}_2^0$, is generally different from, and lower than, the value required by the Debye-Hückel theory at about $0.1 m$. Hence the interaction coefficient λ must vary with temperature, and in such a manner that $(\lambda_{25} - \lambda_0)$ will be positive for strong electrolytes. It is evident from table 3 that this is the case.

For exact calculations one must evaluate the well-known thermodynamic expression

$$(-\log \gamma)_{T_2} - (-\log \gamma)_{T_1} = \int_{T_1}^{T_2} \bar{L}_2 / (\nu RT^2) dT \quad (7)$$

where \bar{L}_2 is a function of the temperature at constant molality. But as a rough estimation for technical purposes, we have found the following semi-empirical equations to be of some value

$$(1-1 \text{ type}) \lambda_{25} - \lambda_0 \pm +0.0002_6 [200 - \bar{L}_2(0.1m, 18^\circ\text{C.})] \quad (8)$$

$$(1-2 \text{ type}) \lambda_{25} - \lambda_0 \pm +0.0004 [600 - \bar{L}_2(0.0333m, 18^\circ\text{C.})] \quad (9)$$

\bar{L}_2 may, for example, be taken from reference 15 or calculated from heat content values given in reference 1, using the procedure described in reference 15 (equation 38).

DISCUSSION

According to Guggenheim (5), the formulas given are applicable not only to such electrolytes as are covered by the original Debye-Hückel theory, but also to those with mean diameters too small to obey the equation of Debye and Hückel. Weak electrolytes are included as long as they are present chiefly as ions (incomplete dissociation also gives a term approximately linear to concentration). Appreciable specific properties of the different electrolytes are taken account of by the present formulas. When the intermolecular forces are so strong, however, as to cause considerable interaction between ions of like sign, some extension of the theory

is necessary. Such strong effects are found, for example, between the picrate anions studied by Lange (11), and between the dipicrylamine anions studied by Kielland (9). Since the London forces (14) are additive¹, such an extension does not seem too difficult.

The Guggenheim theory in its present form is best applicable to inorganic and simple organic electrolytes, with a concentration range up to ionic strengths about 0.1 molal and often higher. The interaction coefficients in table 3 are given so as to correspond to the best measurements at about $\mu = 0.1$ molal; we do not claim that the figures presented are absolutely the most probable ones, and many of them will of course need some revision as better experimental data appear.

SUMMARY

Simple equations (of the Debye-Hückel-Brönsted-Guggenheim type) and parameters with numerical tables are given for some one hundred electrolytes at 0° and 25°C., by means of which osmotic and activity coefficients may be computed for solutions of single as well as of mixed electrolytes. The most accurate and useful concentration range is up to ionic strengths of about 0.1 molal.

REFERENCES

- (1) BICHOWSKY AND ROSSINI: *Thermochemistry of Chemical Substances*. Reinhold Publishing Corporation, New York (1936).
- (2) BRÖNSTED: *J. Am. Chem. Soc.* **44**, 877 (1922).
- (3) DEBYE AND HÜCKEL: *Physik. Z.* **24**, 185 (1923); **25**, 97 (1924).
- (4) DU RIETZ: *Svensk Kem. Tid.* **50**, 13 (1938); *Kort Handbok i pH-bestämning och titrering*, pp. 38-43, Stockholm (1937).
- (5) GUGGENHEIM: *Phil. Mag.* **19**, 588 (1935).
- (6) GUGGENHEIM AND SCHINDLER: *J. Phys. Chem.* **38**, 543 (1934).
- (7) HARNED AND COOK: *J. Am. Chem. Soc.* **59**, 2304 (1937).
- (8) KIELLAND: *J. Am. Chem. Soc.* **59**, 1675 (1937).
- (9) KIELLAND: *J. Am. Chem. Soc.*
- (10) LANDOLT-BÖRNSTEIN-ROTH: *Physikalisch-chemische Tabellen*, 5 Auflage, II and III Ergänzungsband. J. Springer, Berlin (1931 and 1936).
PRENTISS AND SCATCHARD: *Chem. Rev.* **13**, 139 (1933); and other sources.
- (11) LANGE: *Z. physik. Chem.* **177**, 193 (1936).
LANGE AND HERRE: *Z. physik. Chem.* **181**, 329 (1938).
- (12) LEWIS AND RANDALL: *J. Am. Chem. Soc.* **43**, 1112 (1921).
- (13) LEWIS AND RANDALL: *Thermodynamik*. J. Springer, Wien (1927).
- (14) LONDON: *Trans. Faraday Soc.* **33**, 8 (1937).
- (15) ROSSINI: *J. Research Natl. Bur. Standards* **6**, 791 (1931).
- (16) TAYLOR: *J. Phys. Chem.* **31**, 1478 (1927); Guggenheim: *J. Phys. Chem.* **33**, 842 (1929).

¹ In this connection it is interesting to note that the salt error of sulfonphthalein indicators, according to Du Rietz (4), may be additively calculated also in the case of complicated organic anions; thus definite figures are ascribed to each carbon, oxygen, and chlorine atom, to carboxyl groups in different positions, etc.

CATALYTIC ACTIVITY OF INTERMETALLIC COMPOUNDS IN THE GAS PHASE REDUCTION OF NITROBENZENE

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Upon investigation of the literature the authors found no published data on the use of definite intermetallic compounds as reduction catalysts in the vapor phase. Mixed catalysts have been studied but not definite intermetallic compounds.

Thallium, bismuth, and lead have been used by Brown and Henke (2) as catalysts for the vapor phase reduction of nitrobenzene to azobenzene and aniline. Yields of azobenzene as high as 90 per cent were obtained with thallium under specific conditions.

This paper deals with the use of the intermetallic compounds of thallium, bismuth, and lead as catalysts in the vapor phase reduction of nitrobenzene to azobenzene and aniline. A large yield of azobenzene is preferred to one of aniline. The catalysts used were all supported on asbestos, the ratio of catalyst to asbestos being 60:40.

The materials used and general procedure were essentially the same as those used by Brown and Henke (1). Any variations will be discussed with the description of the catalysts. The electric furnaces used were of two types,—one a short vertical furnace and the other horizontal. The horizontal furnace has been described by Brown and Henke (1). The vertical furnace was 30 cm. in height and had a catalytic chamber volume of 63 cc. It was heated by chromel resistance wire and was constructed in a manner similar to the horizontal furnace.

The essential difference in the two furnaces is the time of contact of the reactants with the catalysts. In the horizontal type the reactants are in contact with the catalyst for a longer period of time than in the vertical furnace.

Most of the work done was on a Tl_2Pb catalyst. Samples were prepared by two different procedures. The first procedure was to mix Hammond litharge with thallium oxide (on asbestos) in the ratio to make Tl_2Pb and then to reduce in hydrogen at $265^\circ C$. This catalyst will be referred to as catalyst A¹. The second procedure was to use c.p. lead nitrate in place of litharge, and to precipitate the hydroxides of the metals together in the

presence of the asbestos support. The hydroxides were reduced in hydrogen at 265°C. to give catalyst A². Catalyst B¹, consisting of Tl₂Pb with 10 per cent excess lead, was prepared by procedure No. 1. Catalyst B² consisted of Tl₂Pb with 20 per cent excess thallium; it was prepared by procedure No. 2. Catalyst C¹ was Tl₂Bi with 10 per cent excess thallium. Catalyst C² was pure Tl₂Bi. These catalysts were prepared by mixing bismuth nitrate and thallium oxide in the correct ratio, precipitating the hydroxides together, and reducing at 265°C.

Some of the experiments tried and results obtained are listed in table 1.

TABLE 1
Vapor phase reduction of nitrobenzene

CATA- LYST	COMPOSITION OF CATALYST	NITRO- BEN- ZENE	TEMPERA- TURE	HYDRO- GEN	FUR- NACES*	YIELD IN PER CENT OF THEORETICAL	
						Azoben- zene	Ani- line
		grams per hour	°C.	liters per hour		per cent	per cent
A ¹	10 g. Tl ₂ Pb	3.6	265	7	V	81.1†	8
A ²	3.5 g. Tl ₂ Pb	3.5	265	14	H	57.6‡	20
A ³	3.5 g. Tl ₂ Pb	4.75	260	14	H	53.6§	20
B ¹	3.5 g. Tl ₂ Pb; 10 per cent ex- cess Pb	3.5	257-271	14	H	68.8‡	23
B ²	10 g. Tl ₂ Pb; 20 per cent ex- cess Tl	3.5	240-247	14	H	Trace	99-100
C ¹	10 g. Tl ₂ Bi; 10 per cent excess Tl	2.5-7	240-287¶	14	H	None	44-72
C ²	10 g. Tl ₂ Bi	2.5-7	260-330¶	14	H	None	20-60

* H = horizontal; V = vertical.

† Average of six experiments. More than 96 per cent of azobenzene was obtained in some runs.

‡ Average of six experiments.

§ Average of three experiments.

¶ Maximum yield at 255°C.

SUMMARY

1. The intermetallic compounds of thallium and lead, under the conditions studied, possess the same catalytic power as that of the components; however, their behavior is more like that of lead than that of thallium.

2. The Tl₂Pb made with Hammond litharge gave better yields of azobenzene than that made with lead nitrate.

3. Both the vertical furnace, which gives a short time of contact of reactant with the catalyst, and a low rate of flow of hydrogen are favorable to the production of azobenzene.

4. The experiments show that only slight changes in the method of

preparation of the catalyst and in the procedure of reduction give entirely different results.

5. The catalytic activity of Tl_3Bi , with and without excess thallium, is similar to that of the metals themselves. However, the activity is not as great as the activity of the individual components when used alone.

REFERENCES

- (1) BROWN, O. W., AND HENKE, C. O.: J. Phys. Chem. **26**, 161 (1922).
- (2) BROWN, O. W., AND HENKE, C. O.: J. Phys. Chem. **26**, 631-8 (1922).

NEW BOOKS

Superconductivity. By D. SHOENBERG. 8½ x 5½ in.; 23 figures; 3 tables; 111 pp. Cambridge: The University Press; New York: The Macmillan Company, 1939. Price: \$1.75.

This little book is one of the first of the new series of *Cambridge Physical Tracts*, which will presumably form a companion series to the *Cambridge Tracts in Mathematics*. The author, who is well known for his work at the cryogenic laboratory in Cambridge, has set a high standard for future volumes of the series.

Ideas concerning superconductivity have been revolutionalized since the discovery by Meissner, in 1933, that a superconductor has the properties of a "perfect diamagnetic" (i.e., $B = 0$ inside the specimen) rather than those of a body of infinite conductivity. The author shows how many of the properties of superconductors can be correlated on the basis of a vanishing magnetic field in the superconducting regions. Without going into experimental details, a description is given of the significant results of recent work and, wherever possible, an attempt is made to give a phenomenological explanation. The scope of the volume is indicated by some of the chapter headings: "Magnetic Properties", "The Intermediate State", "The Superconducting Ring", "Thermodynamic Relations", "Superconducting Alloys", "Thin Films". A summary of experimental data is given in an appendix.

JOHN BARDEEN.

About Petroleum. By J. G. CROWTHER. 181 pp. New York: Oxford University Press, 1938. Price: \$2.25.

This excellent little volume is very generally addressed to all of those interested in any way in petroleum, such as motorists, aviators, engineers, housewives, and investors. But the table of contents, showing a range of topics all the way from occurrence, discovery, and production, through distillation, cracking, and hydrogenation, to lubrication, knock, helium, and carbon black, raises the suspicion that it may interest chemists, physicists, and physical chemists as well. The reviewer can confirm this and recommends the book to anyone who wants a guide to and accurate survey of the present status of the hydrocarbon industry.

S. C. LIPP.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 64: Rhodium. 26 x 17 cm.; pp. xx + vii + 153. Berlin: Verlag Chemie, 1938. Price: 20.25 RM.

The present section includes the description of rhodium, except for its history, occurrence, and production, which will be dealt with in a later volume on platinum. The physical and chemical properties of the element and its compounds are fully considered, with the usual complete references to the literature, including the most recent and that published in England and America. Rhodium is described as a white metal similar to aluminum, more reflective for all wave lengths of visible light than platinum or nickel, but less reflective than silver. It is malleable only after suitable treatment at a red heat, but is notably plastic at ordinary temperature. The element shows valences from one to six in its compounds. The metal has a high melting point, about 1966°C. An important use of rhodium in alloy with platinum as thermo-

couples is not dealt with in the present volume, which also does not discuss its use in alloy with platinum as an ammonia oxidation catalyst. A good example of the care taken to include modern work is the full discussion of the sulfides, taken from a publication of 1935. This section of the *Handbuch* is very satisfactory.

J. R. PARTINGTON.

Kurses Lehrbuch der physikalischen Chemie. By H. ULICH. 24 x 15 cm.; xvi + 315 pp. Dresden and Leipzig: T. Steinkopff, 1938. Price: 12 RM.

The author has attempted, by a careful choice of material and by the omission of purely physical sections, to produce a book of moderate size which yet gives a satisfactory view of physical chemistry up to a standard suitable for students of other faculties, such as engineers, physicists, and biologists, and such as will form a basis of further study for chemists. He has been successful in dealing with all the important branches of the subject in a way which is not at all superficial and is in accord with modern requirements. Particular emphasis is laid on thermodynamics, in which the modern methods are used throughout. The approximate calculation of equilibria by a method not previously published, which depends on the choice of suitable mean heat capacities, is noteworthy, and the numerical examples given throughout the book are a special and valuable feature. English and American work is most carefully taken into account, even to the extent of giving the English technical terms, since the author believes that an increasing use must be made in Germany of publications in that language. The short bibliographies at the ends of the sections are well chosen. The only drawback the reviewer can see to the popularity of the book among students who can read German is the use of different fonts of German cursive type for symbols; these are sometimes difficult to distinguish. The book is one that can be warmly recommended as giving in a limited space a very adequate view of modern physical chemistry.

J. R. PARTINGTON.

The Phase Rule and its Applications. By A. FINDLAY. Eighth edition, revised with the assistance of A. N. Campbell. 21 x 14 cm.; xv + 327 pp. London, New York, and Toronto: Longmans, Green and Company, 1938. Price: 12s. 6d.

There is no need to describe the character of this work, which has been a standard book on the subject since the first edition appeared in 1904. In the new edition some material has been dropped, including the experimental appendix, the contents of which can now be found in books on practical physical chemistry, some sections have been modified (e.g., that on intensive drying), and some material has been added. There comes a time when a book needs to be completely rewritten, since the mere addition of footnotes giving references to newer literature cannot keep a book up-to-date. The reviewer feels that, although many sections have been revised, some are in need of extensive revision. This applies, for example, to the sections on the palladium-hydrogen system (which is now quite out-of-date), the iron-carbon alloys, and liquid crystals. The new edition will continue to provide an excellent introduction to the subject, as the former ones did, and when the time comes for a further edition it is to be hoped that the whole text will be dealt with and the book reset. The present edition has been reproduced by the Novographic process and the old and new matter are often clearly distinguishable both in the text and footnotes, the appearance being far from pleasing.

J. R. PARTINGTON.

Photographic Chemicals and Solutions. By J. I. CRABTREE AND G. E. MATTHEWS. 9½ x 6½ in.; 95 figures; 13 tables; vii + 360 pp. 353 Newbury Street, Boston, Massachusetts: American Photographic Publishing Company, 1939. Price: \$4.00.

The authors are members of the staff of the Kodak Research Laboratories and a large part of this book is based upon papers published in various photographic journals by them and their associates over the past twenty years. Some of the material included is found in much the same form in *Elementary Photographic Chemistry* (Eastman Kodak Company). A formulary is included which contains the formulas of only one manufacturer.

All of this does not in the least lessen the value of the work, for the subject is one that has not received the attention which it deserves in recent photographic literature. From the wealth of their experience Messrs. Crabtree and Matthews have made available in one place, conveniently arranged for ready reference, much information which is of value to every serious photographer. They have drawn liberally upon their wide acquaintance with the conditions existing in the laboratories of the professional photographer, the photofinisher, and the motion picture processing laboratory.

The thirteen chapters cover in considerable detail such important phases in the properties of photographic chemicals and the preparation and use of photographic solutions as arrangement of formulas, conversion formulae, mixing apparatus, temperature measurement and control, effect of the water supply on photographic operations, apparatus for the construction of photographic processing apparatus, mixing and using solutions, handling solutions at high temperature, storage and transport of solutions, substitution of chemicals, stains on negatives and prints, cleaning processing equipment, and precautions in handling chemicals.

There are a number of useful chemical tables and a good index.

C. B. NEBLETTE.

Exposés de Photochimie. By W. ALBERT NOYES, JR., PHILIP A. LEIGHTON, AND GERHARD K. ROLLEFSON. 170 pp. Paris: Hermann et Cie., 1938.

Students beginning the study of photochemistry are very fortunate in having available the excellent and modern survey of the basic principles of the subject that are contained in the first two parts of this book. The more detailed discussions of selected topics which are given in the latter part of the book will serve equally well either as illustrative material for students or as critical surveys for more experienced photochemists.

The first section of 45 pages, written in French by W. Albert Noyes, Jr., is devoted largely to those general aspects of band spectroscopy which are of particular importance to photochemistry. The third and fifth chapters of this section contain rather brief discussions of the spectroscopy of a few selected examples of bi- and poly-atomic molecules. The second section of 72 pages, written in English by P. A. Leighton, treats the secondary or thermal steps of photochemical reactions. The second chapter in this section contains a very brief but clear summary of the more important facts and formulas of kinetic theory as applied to reaction kinetics, as well as an interesting account of the methods used in the analysis of complex reactions. The last three chapters of this section are devoted to three classes of photochemical reactions which have been rather carefully studied. The last section of 58 pages, written in English by G. K. Rollefson, consists of a detailed and critical survey of the photochemical reactions of halogens. Because of his own extensive researches in this field, the author's opinions on some of the more controversial topics are of special interest.

In the reviewer's opinion this book is better adapted to class work and the teaching of photochemistry than anything that has appeared in recent years. The authors

have achieved an unusual simplicity and clarity of style without undue sacrifice of accuracy. This book contains no index.

ROBERT LIVINGSTON.

Metallography. By C. H. DESCH. Fourth edition. viii + 402 pp.; 28 plates; 147 figures. London: Longmans, Green and Company, 1937. Price: \$8.00.

Dr. Desch has drastically revised the third edition (1922) of his book so as to take into account many advancements in the field of metallography. Many sections have been rewritten and expanded. This has all been accomplished without sacrificing the general plan developed and tested through years of teaching. Thermal measurements and analysis, microscopical examination, experimental methods of determining metallic structures and properties, questions concerning crystalline growth, diffusion in the solid, electrolytic potential and corrosion, deformation, age-hardening, and the relations between ordered and disordered solid solutions are among the many subjects treated in the book.

The book contains twenty-two chapters, twenty being on various topics in metallography and two, written by G. D. Preston, on theoretical and experimental x-rays. Numerous references to the literature are given in the footnotes. The index contains the names of more than one thousand authors.

This excellent product of Dr. Desch's scholarship and broad experience should serve well as a textbook or as a reference for scientists in both pure and applied science.

H. A. MILEY.

Electrochemistry of Gases and Other Dielectrics. By GEORGE GLOCKLER AND S. C. LIND. 9½ x 6½ in.; 82 figures; 34 tables; xiii + 469 pp. New York: John Wiley and Sons, Inc., 1939. Price: \$6.00.

Few phases of science afford more voluminous material from which to construct a general treatise than does the subject of chemical reactions in the electric discharge; nevertheless, three almost unsurmountable difficulties present themselves: (1) The physics of the electric discharge has not been fully solved. (2) Most of the reactions described in the literature have been carried out under conditions lying somewhere between the straightforward reaction and equilibrium, consequently the results are specific for experimental conditions and difficult to interpret. (3) The mechanism of reaction in the electric discharge is still a matter of conjecture.

Doctors Glockler and Lind, fully realizing these difficulties, have skillfully made of them a virtue in that these very uncertainties have been used to suggest, if not to stimulate, further research. The authors have described the various proposed mechanisms for the electric discharge in gases, but they have in no way limited the continuous usefulness of their treatise by adhering to any concept that may soon become outmoded. In fact it should be said that the subject matter is so arranged that when further facts are discovered they will serve as an extension of the text, rather than as a correction.

The book is divided into three parts. Part I deals with "Typical Reactions in Various Forms of Discharge." Here are described characteristic reactions in the glow discharge, the silent electric discharge, the corona, and the low-voltage arc. Part II is a comprehensive survey of "Chemical Reactions in the Electric Discharge." Reactions involving carbon, nitrogen, hydrogen, oxygen, and many other elements are treated in detail. A historical approach is adopted where consistent with the subject matter. One chapter is devoted to active nitrogen. Such subjects as colloids, vitamins, insulators, lubrication, and flames are discussed. Part III treats the "Physical and Theoretical Aspects of Discharge Reactions." The physics

underlying the electron affinity of atoms and molecules as well as ion mobilities is considered. The production of ions in the electric discharge and during chemical reactions is described at length. Cathodic sputtering is treated from both a theoretical and a practical point of view. The last chapter gives an excellent discussion of the prevailing theories for the mechanism of chemical action.

This is the first comprehensive treatise published on the general subject of chemical action in the electric discharge. It cannot be too highly recommended to both old and new workers in this field of science, since it represents a painstaking survey of the literature presented as growing rather than as a completed study. The text is replete with suggestions for further research. The print and binding are excellent, and errors are few.

A. KEITH BREWER.

Handbook of Chemical Microscopy. Vol. I. Principles and Use of Microscopes and Accessories; Physical Methods for the Study of Chemical Problems. By ÉMILE MONNIN CHAMOT AND CLYDE WALTER MASON. Second edition. 478 pp.; 165 illustrations. New York: John Wiley and Sons, Inc., 1938. Price: \$4.50.

The first edition of Chamot and Mason's *Handbook of Chemical Microscopy* played an important rôle in familiarizing chemists with the manifold applications of the microscope in the chemical field, and doubtless was directly responsible for the introduction of courses in chemical microscopy and microchemistry in more than one American educational institution. The first volume of the *Handbook* now appears in a second edition and will be welcomed by a wide circle of users.

The new edition of Volume I has, in the words of the authors, "been considerably expanded and rewritten in certain sections, such as those dealing with the study of crystals and cryptocrystalline aggregates, fibrous materials, particle size, illumination, photomicrography, and preparation techniques". An entire chapter is devoted to the important subject of microscopical determinations of particle size. Numerous references to the recent literature are given throughout the book.

Anyone doing work in the field of chemical microscopy will find this excellent work indispensable.

E. B. SANDELL.

Feuerfeste Baustoffe silikatischer und silikathaltiger Massen. By CLAUS KOEPFEL. 22.5 x 15 cm.; xvi + 296 pp. Leipzig: S. Hirzel, 1938. Price: 17 and 15.50 RM.

This work deals with the chemistry of a number of refractory materials, excluding all technical description of their production and uses. Although it is nominally confined to silicious materials, a section on basic and neutral refractories is included, with the object of discussing the influence of small quantities of silica on their constitution and stability. The principal phase diagrams of refractory systems are reproduced, although with less discussion than in some other works on the same systems. The illustrations are confined to these and to curves showing the variation of properties with temperature or with composition, neither microscopic structures nor x-ray pictures being reproduced. Much attention is given to reactions in the solid state, especially in regard to the effects of small quantities of foreign substances on the rates of transformation, a matter of great importance for the practical treatment of these materials. For readers who are already familiar with the literature of refractory materials this will probably be the most interesting section of the book. In other respects the ground is well covered by existing works, but the present volume will be found useful for its abundant references to the literature.

C. H. DESCH.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 66: Osmium, mit einem Anhang über Ekaosmium. 26 x 18 cm.; pp. xx + iv + 100. Berlin: Verlag Chemie, 1939. Price: 14.25 RM.

The present section of Gmelin constitutes a nearly complete monograph on osmium. The arrangement follows the usual order, but the sections on the history and occurrence of osmium are omitted, as they are dealt with in the volume on platinum (now published). The properties of the metal and the preparation and properties of its compounds are given in detail. Apart from the oxides and the halogen compounds, the compounds of osmium do not seem to have been very fully studied, although there is a fairly large literature on complex compounds. The technical or other applications of osmium and its compounds are given. Ekaosmium is described as a product of neutron bombardment of uranium; the latest results in this field came too late to be included.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 68: Platin. Teil A, Lieferung 1. 26 x 18 cm.; pp. ii + 145. Berlin: Verlag Chemie, 1938. Price: 16.50 RM.

The present volume deals with the history and occurrence of the platinum metals. The historical section of fourteen pages is of considerable interest and is based on a large literature, some parts of which are not easily accessible. Some of the earlier processes of extraction may still find application in future technology, as anyone who has occasion to consult modern patent literature will know. The technical working of massive platinum is, as usual, ascribed to Wollaston, although it has been stated (Matthey: J. Chem. Soc. 20, 395 (1867)) that it was really worked out in Allen's laboratory by Thomas Cock, whose work was communicated to Wollaston, who has "generally been accorded the credit of having discovered it." The interesting story of the discovery of palladium is given in detail. The bulk of the section is devoted to the occurrence of the platinum metals and is of great value. All the known sources are considered, with statistical and economic details, and there are some valuable sections on the geochemistry of the metals, with maps. The sources in the Urals, Russia, and Siberia make up most of the description and there is a short section on Asiatic sources, the part on sources in Japan being translated from a Japanese manuscript.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 22: Kalium. Lieferung 6. 26 x 18 cm.; pp. xxxvi + 1075-1230. Berlin: Verlag Chemie, 1938. Price: 21.75 RM.

The present section completes the account of the chemistry of potassium and deals mostly with the double salts with the alkali metals. The long section on Rochelle salt is important, the optical, dielectric, and piezochemical properties being considered in detail and illustrated by curves.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 22: Kalium. Lieferung 7. 26 x 18 cm.; pp. xxxviii + 1231-1338. Berlin: Verlag Chemie, 1938. Price: 16.90 RM.

The present section deals entirely with the technical preparation of potassium salts. After historical and economic sections (the latter with useful tabulated statistics of production from 1861 to 1936, from which it appears that Germany and France are now the main producers), the text deals with methods of extraction from the raw materials and the preparation of each of the technically important potassium salts. There are long sections on the treatment of carnallite and kainite, including the working up of the magnesium salts. The text is descriptive and there are no phase rule diagrams. Felspar, leucite, glauconite, cement kiln and blast furnace dusts, sea water and sea weeds are given as sources, and there is a brief section on organic sources, but wood ash and suint do not seem to be included. The present section, it will be seen, is of considerable technical interest. The main emphasis is on the Stassfurt sources, for which more information is available than is the case for some of the other technical sources.

J. R. PARTINGTON.

Reports on Progress in Physics. Volume V. Published by the Physical Society (London). 26 x 18 cm.; iv + 445 pp. Cambridge: The University Press, 1939. Price: 20s.

The present volume of annual reports deals with the same general range of subjects as previous volumes, but the sections on electricity are much shorter and room is found for special topics such as adsorption in solutions, recent theories of the liquid state, plastics, instrumental aids to defective hearing, electric wave filters, cosmic rays, and the teaching of physics in schools. The standard is high, and the aim set out in the preface that the volumes shall be intelligible and interesting to non-specialists and at the same time informative and suggestive to workers in special fields, is perhaps as nearly realized as is possible. Physical chemists will find much to interest them in the present volume.

J. R. PARTINGTON.

The Elements of Physical Chemistry. By F. W. GODDARD AND E. J. F. JAMES. viii + 251 pp.; 67 figures. London: Longmans, Green and Company. Price: \$1.80.

This little book is designed for the study of physical chemistry by students in England who are preparing for Higher Certificate, First Medical, and University Entrance Scholarship Examinations. At the conclusion of each chapter questions and problems are inserted of the kind that might be met in the above-mentioned examinations. There are two hundred and fifty such questions and the answers are given in an appendix. The ten chapters cover the usual topics in a beginning book in physical chemistry: atomic structure; gaseous and liquid states; solutions; osmotic pressure and colligative properties; mass action; thermochemistry; electrolytes; catalysis; and colloids. The treatment is concise. Students in this country should find the extended list of problems with answers valuable in their own study of physical chemistry.

GEO. GLOCKLER.

Electron Optics. By the Research Staff of Electric and Musical Industries Limited. Compiled and written by Otto Klemperer. 8½ x 5½ in.; 84 figures; x + 107 pp. New York: The Macmillan Company. Price: \$1.75.

This volume is the third addition to the new series of the *Cambridge Physical Tracts* and gives an excellent account of a very modern and important topic. The use of electron beams functioning as light rays and their diffraction in electrostatic and magnetic fields opens up an important field of physics. The resolutions already

attained approach molecular dimensions and little imagination is needed to visualize advances in microscopy that appear to be of the greatest importance to many fields of science. Besides the optical use of electron beams, their importance as image transformers in television and as current multipliers is also discussed. The present tract affords a ready means of becoming acquainted with these modern developments.

GEO. GLOCKLER.

A Course of Study in Chemical Principles. By ARTHUR A. NOYES AND MILES S. SHERRILL. Second edition. $8\frac{1}{2} \times 5\frac{1}{2}$ in.; 6 tables; xxv + 554 pp. New York: The Macmillan Company, 1938. Price: \$5.00.

This famous text has been rewritten and rearranged,—a revision that had been contemplated before the death of the late Professor A. A. Noyes. The first five chapters were published in pamphlet form several years ago. The new arrangement is as follows: Chapter I. Chemical substances in general; Chapter II. The first and second law of thermodynamics; Chapter III. Gases and kinetic theory; Chapter IV. Solutions and molecular theory; Chapter V. Solutions and ionic theory; Chapter VI. Reaction rates; Chapter VII. Chemical equilibrium; Chapter VIII. Phase rule; Chapter IX. Free energy values. The last chapter includes a short discussion of the third law of thermodynamics and calculations of free energy values from spectrographic and heat data. These modern developments might have been rendered in a more extensive manner.

The method used in the first edition, of teaching the fundamental laws and propositions of physical chemistry by means of problems is retained in the second edition. This procedure puts the burden of presentation upon the reader and student. Any individual who will work through the many excellent problems will be amply repaid for his efforts, for he will have covered the subject of physical chemistry in a thorough and complete manner. It is evident that no person in any way even remotely interested in the subject of physical chemistry can afford to omit this volume from his "must purchase" list of books for his library. The notation used agrees in many respects with the one employed by Lewis and Randall. The book is an excellent text for students in physical chemistry and advanced courses and is to be highly recommended for the clear and precise presentation of an intricate subject.

GEO. GLOCKLER.

Proceedings of the Indian Academy of Science. Jubilee Volume of original papers presented in commemoration of the fiftieth birthday of Sir C. V. Raman.

The volume contains thirty-eight papers by various authors and has been collected in commemoration of the fiftieth birthday of Sir C. V. Raman. Most of these papers pertain to the subject of the Raman effect, the theory of small vibrations, force constants, diffraction of light by supersonic waves, etc. Some are concerned with quite different topics having no connection with the general theme. The papers are written in English, French, German, and Italian. The volume should be of interest to research workers in the field of the Raman effect.

GEO. GLOCKLER.

Principles of Flotation. By IAN W. WARK. 101 figures; 39 tables; 346 pp. Melbourne: Australian Institute of Mining and Metallurgy, 1938. Price: 21s.

From Australia, cradle of froth flotation, site of the first agglomerate tabling, and early user of skin flotation (DeBavey), comes now the best book yet written on froth flotation. The author was the first to publish anything on the modern cationic collectors which have made possible reliable flotation of silicate minerals. The

smallest continent has made some of the biggest contributions to the concentration of minerals by filming methods.

Here is a truly critical and discerning book on the principles of flotation, summarizing not only the voluminous literature from the author's own laboratory but thoroughly digesting other work,—American, British, German, and Russian,—as no one has ever done it in English.

The author has been for some years in charge of the flotation research laboratory of the Department of Chemistry of the University of Melbourne. This is financed by a group of Australian metal producers, together with the Burma Corporation, Ltd. His papers in the technical press have always been valuable and independent.

Physical chemistry as a tool in research has long shown its value, but too few of the previous experimenters have been properly equipped with this tool. Dr. Wark so saturates his argument with physicochemical concepts that he excels Gaudin, who has previously stood out in this respect, and he rivals Gaudin in clarity of exposition. The charts are numerous in which Wark uses various flotation results as functions of pH, thus expanding the work initiated by Gaudin. The chapter on depressants is the best one in the book and is a fine critique from the physicochemical standpoint.

Such an encomium does not mean that the writer has not erred nor that his standpoint is not debatable. The eras in growth of flotation theory are not shown, and the effort seems to have been to present a picture of the best present flotation theory. Historical sequence is usually lacking. The pioneers are forgotten or go uncredited. During the era of "oil" flotation, and especially between 1912 and 1917, the temperamental process of froth flotation was converted from one applied to only a few hundreds of thousands of tons of ore per annum to a reliable process working on over 50,000,000 tons per annum in America and as much in the rest of the world. The author entered the flotation picture only after the swing from oil flotation to soluble collectors had been well accomplished and the theories built around "oil" had been adapted to the new reagents. Perhaps this excuses his lack of appreciation of the earlier work.

The importance of contact angle measurements is emphasized, but the author does not credit T. J. Hoover, who wrote the very first book on flotation nearly thirty years ago, with giving like emphasis. Methods of measurement in Hoover's day were not so elegant as the present ones and did not tell us as much. On the other hand, credit is claimed for Bradford in first activating sphalerite for flotation by treatment with copper sulfate. Bradford has an Australian patent dated 1913 and this would appear to justify the claim. Nevertheless, the American J. F. Myers and his associates made their separate discovery in Tennessee in July, 1914, and put it into commercial practice. Their historic bronze-slide testing machine gave better results than the commercial wood and iron machine and led to its widespread commercial use in the United States with no knowledge of the existence of the Bradford patent.

The connection with flocculation of the floated mineral with good conditions of flotation is credited to Sulman (1919) and Edser (1922) on pages 26, 146, and 301. Closer study of the literature would reveal that in America Bancroft and Van Arsdale were making these observations in 1916-17. The author states in oracular fashion that flocculation of the floated minerals is only a concomitant to and not a necessary antecedent to flotation. He says that mineral particles clinging to air bubbles give pseudo-floccules. The reviewer knows that the quality of a good practical working froth of just the right volume and lasting just long enough to get out of the machine is quite closely connected with flocculation condition in the froth, and the author's

review of the paper stating these facts has missed the point. It is agreed that proper preparation of an ore pulp involves gangue dispersion to release valuable minerals from complex floccules and to remove slime coatings from mineral surfaces. Thereafter the attempt is to attain selective flocculation even though nothing but "pseudo-floccules" might be formed. The condition of flocculation is the beginning of water repellance.

The final chapter of the book is on electrical theories of flotation and is the finest thing yet written on this subject. It recalls the suggestion by the present reviewer made in 1914 that a study should be made of surface charges of suspended particles in their relation to flotation. Swarms of tyros sought to climb enthusiastically onto the electrical bandwagon, only to have it break down. A disgraceful series of incompetent papers was written. Wark points out the true nature of the electrokinetic potential (a term of recent coinage) but draws an incomprehensible conclusion that, because an air bubble when it attaches itself to a mineral particle displaces the film of water on a portion of the mineral surface, only the electrochemical potential is of importance. Surface energy simply must have electrical manifestations and, without getting into the hen-and-egg argument, the reviewer must insist that we are not through with "electrical" theories.

The non-sulfide and non-metallic minerals are mentioned casually in many places but emphasis is given to flotation of sulfide minerals. Too little is known to permit the author to discourse extensively on the non-metallics.

Flotation reagents are classed as frothers, collectors, activators, and depressants. Modifiers and dispersants are rejected as unnecessary. The reviewer cannot agree. If a dispersant causes removal of a slime coating, the resulting flotation cannot be said to be due to activation by the dispersant; the latter removed an impediment that was in the way of the true activator. Incidentally, no mention is made of the original classification of frothers and collectors that seems to have come from the group at the Mellon Institute backed by J. M. Callow in 1915-17.

An exceedingly useful book has been presented and the reviewer is justified in stating that one of the brightest stars has flashed into the flotation firmament. Dr. Wark should be encouraged to continue his excellent work.

OLIVER C. RALSTON.

Inorganic Colloid Chemistry. Vol. III. The Colloidal Salts. By H. B. WEISER. viii + 473 pp. New York: John Wiley and Sons, Inc., 1938. Price: \$6.00.

This volume completes Professor Weiser's important work on the colloid chemistry of inorganic substances. The book gives an excellent summary of the recent work in the borderline field between the colloidal state of salts and their precipitated form or macroscopic state. The subject falls rather naturally into five parts, and the author considers the colloidal (1) sulfates, (2) halides, (3) sulfides, (4) ferrocyanides and ferricyanides, and (5) silicates in the order named. The section on sulfates also includes a chapter on carbonates, phosphates, chromates, and arsenates.

Throughout the book the importance of the adsorption of many different kinds of ions is stressed. This leads to discussions of mechanisms of adsorption, electrical effects, stability, sensitization, coagulation, contamination of precipitates, adsorption of indicators, etc. Thus a good deal of the colloidal chemistry of sols is presented whenever the author is able to connect it with the results of studies on the salt under consideration. In addition, the important bearing which much of the work in this field has on analytical chemistry is emphasized. The value of some of these materials in the industrial field and in everyday life is shown by consideration of the setting of gypsum, and the preparation and properties of lithopone. Separate chapters are devoted to (1) the silver halides in photography, (2) inorganic soil

colloids, and (3) cement. This volume brings the subject matter up-to-date and gives a good picture of the state of the science at this time. However, the work is more factual than critical. There are some errors in the book and authors' names are sometimes misspelled.

The complete three-volume set on inorganic colloid chemistry constitutes an important addition to the English works in the field of colloids. Investigators in the many phases of the subject will find Professor Weiser's contribution both useful and valuable.

L. H. REYERSON.

Physicochemical Experiments. By ROBERT LIVINGSTON. 70 figures; xi + 257 pp. New York: The Macmillan Company, 1939. Price: \$2.25.

The avowed primary object of this attractive appearing laboratory manual is to set forth a course illustrating basic principles. In addition, the experiments and procedures have been so chosen as to give the student familiarity with the more common and important apparatus and techniques. In the conduct of the experiments and treatment of results, a quantitative point of view is fairly uniformly maintained.

The practice of having apparatus set up in advance for the student is regarded by the author as justifiable when the apparatus is complicated, but he feels that "its general use seems ideally adapted to discourage any initiative or sense of responsibility which the student may possess." Accordingly the apparatus and procedures are described and illustrated in sufficient detail so that the student should be able to set up and carry through the experiments himself without much assistance. The details are, however, not of such a character as to rob the work of interest.

A useful feature of the book is the inclusion of general directions for performing a number of laboratory manipulations which have utility apart from that in the experiment under discussion. These include such things as the method of setting a Beckmann thermometer, the preparation and use of a thermocouple (incidentally more ice is needed on the cold junction, Fig. 48), use of the tablet press, use of the polarimeter, and the like. Frequent references are given to other books for further details.

Another useful feature is the inclusion, occupying the first fifty pages, of a good, simple discussion of computing methods and the theory of errors of measurement. These matters should be studied at some time by every science student.

Forty-one experiments are described, a number of which are new, at least to the reviewer. Under each experiment is given a brief statement of the more pertinent theory involved, with definite references to well-known texts for more complete treatment. Then follows a list of apparatus and materials, and an apparently adequate section on procedure. Finally the treatment of results is briefly indicated with, however, most details of this matter intentionally left to the student.

Those who have need of a laboratory manual of physical chemistry should certainly give consideration to this book.

ROSCOE G. DICKINSON.

The Fine Structure of Matter. Volume II, Part II: Molecular Polarization. By C. H. DOUGLAS CLARK, D.Sc., A.R.C.S., A.I.C., D.I.C.; Assistant Lecturer in Inorganic Chemistry in the University of Leeds. 14.5 x 22.5 cm.; lxxii + 241 pp.; 35 figures. New York: John Wiley and Sons, Inc., 1938. Price: \$4.50.

This second of the three parts which constitute Volume II of *A Comprehensive Treatise on Atomic and Molecular Structure* treats primarily refraction, dielectric constant, and dipole moment and their relation to molecular structure and, in so,

doing, discusses molecular association, adsorption, electric double refraction, and molecular fields, devoting a brief chapter to the latter subject. The book is handicapped at the start by the fact that it treats nothing in the literature published after the latter part of 1934, being, in consequence, already four years out-of-date in the presentation of a subject which has developed largely during the past twelve years. Although the references are by no means complete for the period covered, such emphasis is placed upon the abstracting of papers, about a thousand references being given, that many of the pages read like highly condensed versions of an abstract journal. The material is often not well correlated and sometimes appears quite undigested, little or no distinction being made between obsolete and inaccurate data and new and dependable information.

For a description of methods of measuring dielectric constants reference is made to a review published twelve years ago. The statement is made at the bottom of page 227 that the dielectric constant "diminished with increasing pressure," while it would certainly be expected to increase with increasing pressure and was actually found to do so in the work with reference to which this statement is made. It seems unnecessary to complicate our phraseology with "relaxion time" instead of the generally used "relaxation time". The most important step in the derivation of the Clausius-Mosotti expression on page 257 is omitted, as is the derivation of the Debye equation, which seems to present little mathematical difficulty. On page 269 abnormalities in the behavior of acetic acid vapor, which were actually caused by molecular association, are attributed to a statistical distribution of the molecules among different vibrational states, as erroneously proposed in the original paper, while, on page 349, a subsequent paper by the same author is reported as attributing the same abnormalities to changing degree of association. The interchange of the usual ordinates and abscissae in plotting the polarizations of liquid mixtures against concentrations is slightly confusing to one accustomed to the common procedure, but the use of old data which show only approximately the form of the curve for benzene-alcohol mixtures is open to more serious criticism. On page 343 in a table of the moments of the alkyl halides the values given increase markedly from methyl to ethyl in the fluorides and chlorides and decrease slightly in the bromides and iodides. The author concludes "there is no appreciable increase in dipole moment with increasing chain length, except possibly from methyl to ethyl in the fluoride and bromide series," although his figures show a slight decrease in the bromide series. Actually, the data in the literature, available even in 1934, show a considerable increase in moment from methyl to ethyl in all four series. On page 347 it is stated that no noticeable dependence of moment on temperature was found in diethyl succinate, while, actually, a large variation with temperature was observed in solution. In the table of disubstituted benzenes on page 361 the moment of the amino group is incorrectly treated as acting in the plane of the ring. These and other inaccuracies are far more serious than the not always avoidable slips, such as writing the formula of methyl alcohol as CH_2OH in figures LX and LXI or giving the number of a figure incorrectly as on page 320.

No one can fail to approve of the aim of this treatise and the reviewer is certainly cognizant of the many difficulties that beset the path of its author and is sympathetic with his efforts to overcome these difficulties. Unfortunately, it is not possible to report that these efforts have been successful in this second part of the second volume. The book cannot be recommended to the beginner because of its lack of clarity and occasionally of authority and accuracy in the presentation of the material. The reader having some knowledge of the subject will almost certainly find facts and references that have previously escaped his attention, but he will probably find more in the course of a day or two spent with a good abstract journal.

CHARLES P. SMYTH.

The Fine Structure of Matter. Vol. II, Part III: The Quantum Theory and Line Spectra. By C. H. DOUGLAS CLARK, D.Sc., A.R.C.S., A.I.C., D.I.C.: Assistant Lecturer in Inorganic Chemistry in the University of Leeds. 14.5 x 22.5 cm.; lxxii + 184 pp. New York: John Wiley and Sons, Inc., 1938. Price: \$4.50.

This book constitutes the third part of the second volume of the *Comprehensive Treatise on Atomic and Molecular Structure*, which is in the course of publication by the author. Since it is the stated intention to make the separate portions of the work reasonably complete individually, we shall consider the portion under review by itself, rather than as a part of the larger work.

The scope of the text is much more restricted than might naturally be assumed from the title, being concerned primarily with the classification of the electronic states of atoms and ions by means of the vector coupling model. The discussion of multiplet structures is carefully done, and many useful diagrams and tables are included, but the reviewer feels that the book leaves much to be desired as a survey of the field of line spectra. For example, the whole problem of intensities (except for the simpler selection rules) is summarily discussed in four pages (§ 59), while hyperfine structures and nuclear spin angular momenta are not discussed at all. This is probably due in part to the circumstance that the author gives no theoretical discussion beyond a brief treatment of the Sommerfeld fine-structure formula on the basis of the Bohr theory. As a consequence the whole tone of the book seems unnecessarily "old quantum theoretical."

While these limitations severely restrict the usefulness of the book for reference purposes, it will probably be of considerable help to those readers who wish to learn something of the actual details of atomic energy states, but who do not wish to tackle the more comprehensive treatments of Sommerfeld or Grotrian, or the extensive theoretical discussion of Condon and Shortley. For the physical chemist this study will undoubtedly become of increasing importance in the future as the problem of relating chemical valency to atomic states becomes clearer, since it is not possible to understand valency from a knowledge of the ground states, alone, of the atoms and ions.

F. HILL.

Advanced Experiments in Practical Physics. By J. E. CALTHROP. 22 x 15 cm.; xix + 121 pp. London: Heinemann, 1938. Price: 8s.6d.

It is by no means an easy task to devise an advanced practical course for final honours students in physics that shall be both an illustration of the principles of the subject and an adequate training in the use of the hands. Students are, one feels, too frequently presented with pieces of apparatus that require little or no setting-up in order to give the required results. In *Advanced Experiments in Practical Physics* Mr. Calthrop has overcome these difficulties to a large extent. Nearly fifty excellent experiments in properties of matter, heat, light, and electricity have been collected, and the book is to be recommended to student and teacher alike. The experiments are clearly explained with the help of 170 diagrams, and a sound balance between the older and newer branches of physical knowledge has been maintained. Where necessary, references to original papers or more complete accounts have been given. Apart from its value as a guide to experimental work, the book forms in many instances an appropriate supplement to the lecture course, and students in laboratories which do not possess the whole of the equipment necessary will profit considerably from the reading of Mr. Calthrop's clearly written volume.

J. T. RANDALL.

ELECTRO-ULTRAFILTER FOR INDUSTRIAL USE

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Some years ago we gave a description of an electro-ultrafilter (1). This apparatus was intended for a capacity of 500 cc. The production of

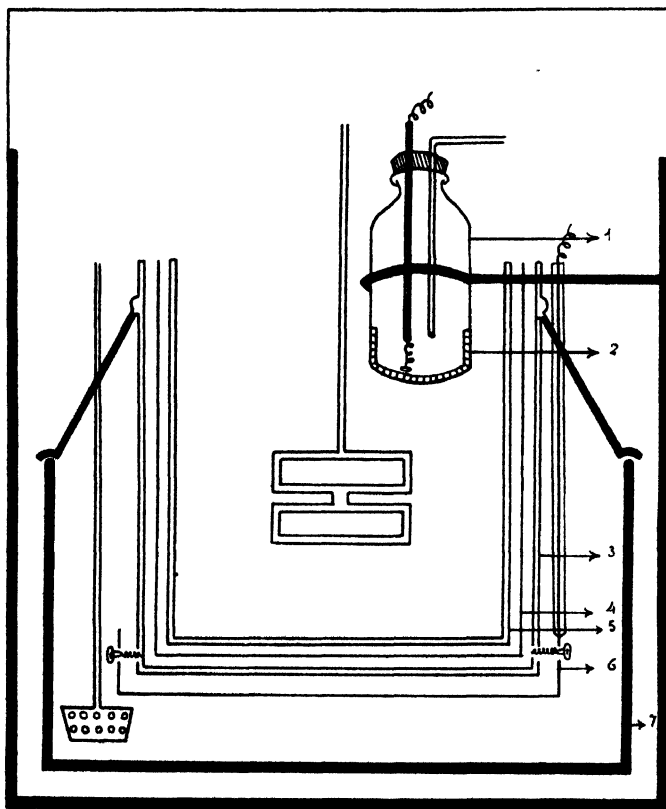


FIG. 1. Electro-ultrafilter. 1, suction receiver; 2, layer of collodion; 3, receiver for serum; 4, parchment bag; 5, glass bars; 6, silver electrode; 7, receiver for water.

serum for therapeutic use by means of electrodialysis is not only an economy of time, but it is also, from the medical point of view, of great advantage because of the thorough elimination of the euglobulin and the

other labile and therefore, from the immunologic standpoint, unnecessary albumins (2). For these reasons we have constructed an electro-ultrafilter of greater capacity. The apparatus has worked satisfactorily in the concentration of sera. Its construction is shown in figure 1.

For the reception of the serum a container (3) of porcelain is used, which has the form of a tumbler and is of 5-l. size. The bottom of this receiver is unglazed, but the walls are glazed. A well-fitting parchment bag (4) is placed in this receiver. In order to keep the parchment close to the wall of the receiver, a basket-like support (5) made of glass bars is used. For the first filtration and for the removal of the water, a smaller receiver is used, also with unglazed bottom. This smaller receiver (1) is supported in such manner that only two-thirds of it is placed in the larger one. The lower part of the outside of this smaller receiver is covered with a layer of a 10 per cent solution of collodion in glacial acetic acid. The top of it is hermetically sealed by means of a rubber stopper, containing two holes; through one hole the electrode passes, while the second is connected with a vacuum. The electrode consists of a platinum wire grating, with a platinum spiral, over which a glass tube is fused. The spiral is used for the purpose of passing the electrode to the bottom of the receiver. This is important, as the diameter of the anode is very small in proportion to that of the cathode. The cathode consists of a perforated silver plate,¹ the diameter of which is fastened by means of a rubber ring below the bottom of the larger receiver. The connection between the silver plate and the rubber ring must be made in such a manner that one can change the depth at which the electrode is suspended in a water reservoir. Naturally the water as well as the serum must be stirred constantly.

By means of this apparatus the volume of a previously dialyzed solution of pseudoglobulin can be reduced to 10 to 15 per cent in 24 to 36 hr. and the electroconductivity can be diminished to 10^{-5} reciprocal ohms

REFERENCES

- (1) KLOBUSITZKY, D. v.: *J. Phys. Chem.* **36**, 3189 (1932).
- (2) KLOBUSITZKY, D. v.: *Ergeb. Hyg. Bakt. Immunitätsforsch. Exptl. Thérap.* **22**, 238 (1939).

¹ Brass can be used instead of silver, the most advantageous form being a brass grating.

THE MAGNETIC PROPERTIES OF INTERMEDIATES IN THE REACTIONS OF HEMOGLOBIN¹

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The theory of the oxygen equilibrium of hemoglobin proposed by Pauling (10) in 1935 treats the existent data quantitatively in terms of equilibrium constants for the stepwise oxygenation of hemoglobin, and introduces theoretical relations between successive equilibrium constants. This theory is here applied in detail to the oxygen equilibrium, and the calculated concentrations of the intermediate compounds as a function of the degree of oxygenation are presented in a figure. These calculations furnish a new point of departure for the examination of physicochemical studies of the hemoglobin-oxyhemoglobin system and of systems similar in nature, such as the hemoglobin-carbonmonoxyhemoglobin system and the hemoglobin-nitric oxide hemoglobin system.

The experimental portion of this investigation consists of titration studies of two systems, involving complex formation of hemoglobin with oxygen and with nitric oxide, for which the magnetic properties have been followed as a function of the degree of completion of the reaction. These measurements show that the values of the magnetic susceptibility of the intermediate compounds formed during these reactions are linearly related to the number of hemes that have undergone reaction. The observations make it possible to reject one structural explanation of the magnetic moment of ferroheme, namely, that each iron atom has two unpaired electrons and that the spin moments of the four iron atoms of the molecule are brought into alignment by chemical forces operating between the hemes; and they thereby strengthen the conclusion reached by Pauling and Coryell (12) that the iron atoms have four unpaired electrons each and are held in the hemoglobin molecule by bonds that are essentially ionic.

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I. INTERMEDIATES IN HEMOGLOBIN COMPOUND FORMATION

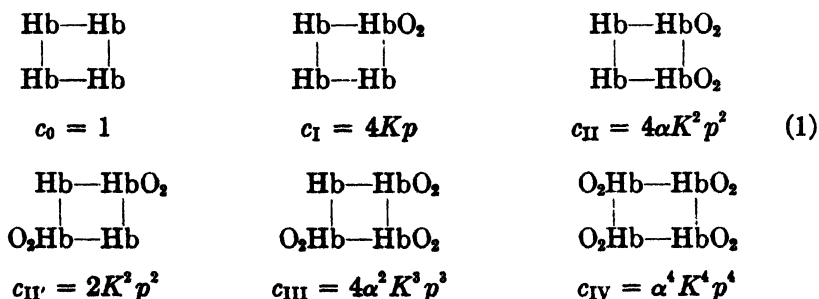
Physicochemical studies of compound formation of ferrohemoglobin with oxygen and carbon monoxide have shown that the reaction does not correspond to a simple equilibrium between each individual heme group (Hb) and the reacting substance. It is now known that under ordinary conditions in aqueous solution there are four iron-porphyrin complexes in a hemoglobin molecule (Hb_4), with molecular weight close to 67,000. Adair (1) and Ferry and Green (7) have shown that the oxygen equilibrium of purified hemoglobin solutions can be interpreted quantitatively by taking into account the existence of the intermediate oxygen compounds Hb_4O_2 , Hb_4O_4 , and Hb_4O_6 , as well as Hb_4 and Hb_4O_8 , and they have determined equilibrium constants for each step of the reaction, obtaining an equation which represents empirically the overall oxygen equilibrium. Equilibrium measurements on defibrinated whole blood and on corpuscular suspensions have similarly been explained satisfactorily by the postulate of the existence of intermediate compounds. These measurements indicate the same molecular complexity for hemoglobin in its natural state in the erythrocytes as in solution with various buffers. It is to be noted that convincing evidence for the existence of intermediate compounds in hemoglobin reactions is provided by the studies by a number of observers of equilibria of hemoglobins of various species, in whole blood and in solutions of various concentrations and at various pH values, with oxygen and carbon monoxide; and that the theory of intermediate compounds gives the only explanation of the experimental data that is compatible with the degree of aggregation (Hb_4) of hemoglobin.

Pauling in 1935 (10) analyzed the extensive measurements of Ferry and Green (7) on horse hemoglobin and showed that the results are compatible with the assumption of interactions operative between the heme groups in such a manner that the free energy of oxygenation of one heme group is decreased by $RT \ln \alpha$ when an adjacent heme group is already combined with an oxygen molecule. Two spatial arrangements of the hemes were considered in detail,—(a) at the corners of a square and (b) at the corners of a tetrahedron. The latter possibility was rejected, because it would require the heme groups to be some 47 Å. apart on the surface of the globin molecule and because it would require each heme to be bonded to three others, which is rendered improbable by the known structure of the porphyrin molecule. From the dependence of the oxygen equilibrium constant of the heme on acidity it was also concluded that acid groups whose ionization constants are increased by oxygenation are coupled with

the heme groups. The total heme-heme interaction energy in the molecule was found to be about 6000 cal. per mole, and the total heme-acid group interaction energy about 6600 cal. per mole. Assuming the square arrangement of hemes, the heme-heme interaction energy corresponds to the value 12 for the factor α , which represents the increase in the equilibrium constant of the heme-oxygen reaction when an adjacent heme is already in combination. We shall use the name *interaction constant* for α .

Many experimenters have tried to find direct evidence for the existence of the intermediate compounds in reactions such as that of oxygenation. (See, for instance, the paper of Conant and McGrew (4).) The interest in these investigations and the importance of outlining the precision with which experiments must be made in order to test directly the interaction theory make it desirable to calculate the concentrations of the various intermediates in the oxygenation of hemoglobin at various stages of the reaction, as predicted by this theory. The equations used in the calculations will be derived below. It is convenient to make the calculations for horse hemoglobin, assuming square configuration of the heme groups⁴ and the experimental value 12 for α as determined from the data of Ferry and Green on horse hemoglobin. It is not unlikely that the numerical value of the interaction constant α will be found to vary somewhat with the nature of the globin, since the interaction system probably involves the protein molecule as well as the prosthetic group.

The relative concentrations of the two end substances and the various intermediates are given at constant acidity by the following values, with the concentration c_0 of Hb_4 taken as standard at unity:



⁴ We have also made calculations of the concentrations of the various intermediates in the oxygenation of hemoglobin, assuming the tetrahedral configuration of the hemes. These calculations give nearly the same results as those given below for the concentrations of Hb_4 , Hb_4O_2 , Hb_4O_4 , and Hb_4O_6 , but the concentration of the dioxy intermediate Hb_4O_4 is approximately two-thirds as great throughout the whole range. We know of no measurements sufficiently precise to distinguish between these two possible configurations, and we shall restrict ourselves to consideration of the square configuration as the more probable one and as a close approximation to the truth unless new evidence conflicting with this is brought to light.

The numbers 4, 4, 2, and 4 are the statistical weights of the intermediates (the numbers of ways in which the oxygen molecules can be added to the hemoglobin molecule to give the intermediates). The symbol p represents the oxygen pressure, in millimeters of mercury, and K the equilibrium constant for oxygenation of an isolated heme, as defined by the equation

$$\frac{(\text{HbO}_2)}{(\text{Hb})} = Kp \quad (2)$$

Its value is dependent on the acidity of the solution (10). The relative concentration of an intermediate is increased α -fold for each pair of adjacent hemes contained in the molecule, independent of the acidity.

With consideration of the oxygen content of each molecular species, the values for the relative concentrations given in equation 1 lead to the following equation for the fraction of saturation, y , as a function of the oxygen pressure:

$$y = \frac{Kp + (2\alpha + 1) K^2 p^2 + 3\alpha^2 K^3 p^3 + \alpha^4 K^4 p^4}{1 + 4Kp + (4\alpha + 2) K^2 p^2 + 4\alpha^2 K^3 p^3 + \alpha^4 K^4 p^4} \quad (3)$$

This equation, with the value 12 for α , represents very well the observations of Ferry and Green.

From equations 1 and 3 there can be derived expressions for the concentrations of the molecular species as functions of the fractional saturation with oxygen. The concentration of a given species for a given value of Kp is divided by the sum of all concentrations to give a normalized value; curves representing these quantities are plotted against y in figure 1. The values of the ordinates in figure 1 give, accordingly, the fraction of the hemoglobin molecules existing in a given oxygenation step for the corresponding values of the overall saturation plotted as abscissas.

This theory of the effect of hemoglobin structure on physicochemical relationships accounts for the characteristic sigmoid saturation curves of hemoglobin solutions and whole blood with oxygen and carbon monoxide in the following manner: At very low oxygen pressures the principal oxygen compound must be the monoxy compound. The formation of the *cis*-dioxy compound is made easier than would be expected from statistical calculations for independent hemes, because it contains a pair of adjacent oxyhemes which stabilizes the molecule by the amount of free energy $RT \ln \alpha$, and consequently the hemoglobin solution takes up oxygen more readily after an appreciable amount of monoxy compound has been formed than at the start of the reaction. This causes the upturn of the oxygen saturation curve in the early stages of the reaction. The trioxy compound is stabilized over the *cis*-dioxy compound by the same amount that the *cis*-dioxy compound is stabilized over the monoxy compound, whereas the tetroxy compound is doubly stabilized over the trioxy compound because

it has four interacting pairs of hemes instead of two; this compound becomes of importance even early in the reaction, and its stability accounts in the main for the rapid approach of the sigmoid saturation curve to the asymptotic value. It is seen that at half-saturation 34 per cent of the hemoglobin is in the form of intermediates.

The saturation curve of carbon monoxide with hemoglobin is also sigmoid; and the relatively few experiments that have been reported indicate that the degree of sigmoid character is very close to or identical with that for the oxygen curve (see the curves of Douglas, Haldane, and Haldane (6) for oxygen and for carbon monoxide). Further qualitative evidence for the close similarity in degree of sigmoid character of the two curves is

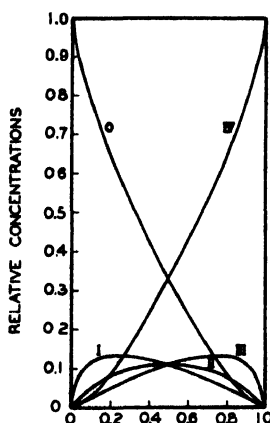


FIG. 1. Concentrations of molecular species as functions of degree of oxygenation of horse hemoglobin. 0 = Hb_4 ; I = Hb_4O_2 ; II = *cis*- Hb_4O_4 ; III = Hb_4O_6 ; IV = Hb_4O_8 . The curve for *trans*- Hb_4O_4 is not given; it has one twenty-fourth the height of II throughout.

found in the study of the reaction between oxyhemoglobin and carbon monoxide (6), in which the hemes appear to act independently. If α for the carbon monoxide equilibrium of horse hemoglobin is equal to that for the oxygen equilibrium, figure 1 is directly applicable to the distribution of molecular species in the carbon monoxide equilibrium; it is in any case applicable as a fair approximation.

Since nitric oxide hemoglobin has structure and physical properties nearly like those of oxyhemoglobin and carbonmonoxyhemoglobin, it is probable that its equilibrium with hemoglobin also can be represented approximately, if not exactly, by equation 3 and figure 1.

Figure 1 may be used in general in correlating with the degree of reaction properties of hemoglobin which are affected by reaction with complex-

forming molecules. These properties may include magnetic susceptibility, base-binding capacity, chemical reactivity, heat of formation, and others.

II. MAGNETIC TITRATIONS INVOLVING FERROHEMOGLOBIN

The value of the magnetic susceptibility of cow hemoglobin at 25°C. has been redetermined by Taylor and Coryell (13) and found to be $4 \times (12,290 \pm 60) \times 10^{-6}$. It was found that the magnetic susceptibilities of horse and sheep hemoglobins have the same value, to within the experimental errors of their determination, whereas that of human hemoglobin is about 3 per cent lower.

Pauling and Coryell (12) discussed in a structural interpretation of the magnetic properties of ferrohemoglobin compounds two alternative possibilities, I and II, in explanation of this value. It was assumed as hypothesis I that the chemical interactions between the ferrohemes are strong enough to couple the magnetic moments of the four iron atoms into a resultant moment, and that each iron atom contributes two unpaired electrons, leading to a magnetic moment for the hemoglobin molecule of 8.95 Bohr magnetons plus about 10 per cent orbital contribution,⁵ or, roughly, 10 magnetons. This value is to be compared with the value 10.87 magnetons calculated from the experimental value of the susceptibility of the hemoglobin molecule, assuming the conditions of hypothesis I. As the alternative hypothesis II, it was assumed that the iron atoms are independent in their magnetic behavior, leading to a predicted moment per heme group of 4.90 plus orbital contribution. This is to be compared with the value 5.44 calculated from the experiments assuming the conditions of the hypothesis. (Observed values for ionic ferrous compounds are about 5.1 to 5.3 magnetons.) Hypothesis II was accepted as the more probable one by these workers, partly because of the results of experiments preliminary to those presented in this investigation.

We shall explore the first possibility further. We assume that each ferroheme group contributes two unpaired electrons to the total number, and that unpaired electrons are coupled with parallel moment vectors for ferroheme groups. We expect then for a series of compounds involving

⁵ The magnetic moments of the iron group elements are due principally to the spin moments of unpaired electrons. The total spin moment, μ_s , is given by

$$\mu_s = \sqrt{n(n+2)}$$

where n is the number of unpaired electrons. The orbital contribution to the magnetic moment is nearly completely quenched, but enough remains to raise the value of the magnetic moment somewhat (for elements with more than five electrons in the 3d levels), by amounts that as yet cannot be predicted accurately, since they depend on chemical environment as well as on the spectroscopic term value of the paramagnetic atom.

transformation of hemes from paramagnetic to diamagnetic, such as for the series Hb_4 , Hb_4O_2 , Hb_4O_4 , Hb_4O_6 , and Hb_4O_8 , spin moment values of $\sqrt{80}$, $\sqrt{48}$, $\sqrt{24}$, $\sqrt{8}$, and 0. We make the assumption, reasonable for such a series of closely related compounds, that the orbital moment persisting⁵ is a constant fraction of the total spin moment. The value of the molal paramagnetic susceptibility for each of these compounds, which is directly proportional to the force determined by the Gouy method, is proportional to the square of the moments (given above) for them.

Since measured magnetic susceptibilities are proportional to concentration and are additive, the magnetic susceptibility of a hemoglobin solution

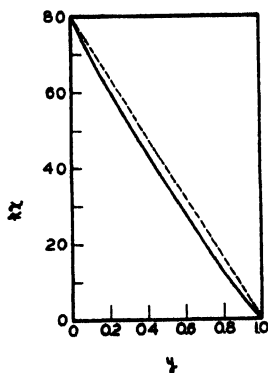


FIG. 2

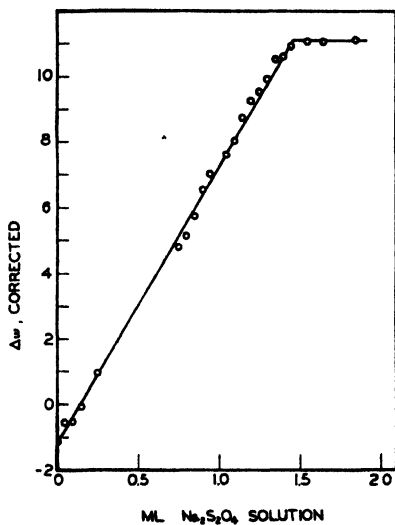


FIG. 3

FIG. 2. Predicted magnetic susceptibility of a hemoglobin solution as a function of degree of saturation with oxygen.

FIG. 3. Magnetic titration of oxyhemoglobin solution with sodium hydrosulfite solution. Run No. 1.

as a function of the degree of saturation, y , with a compound giving diamagnetic iron atoms can be predicted from these values for molal susceptibilities and the values for concentrations of various hemoglobin derivatives given in figure 1. A plot of the predicted dependence of the susceptibility $k\chi$ on y is given in figure 2.⁶ The solid curve represents the predictions for hypothesis I with complete magnetic interactions, and the dashed line that for complete magnetic independence of the hemes. It is seen that at $y = 0.5$ the magnetic susceptibility would be 11 per cent

⁶ The assumption of tetrahedral heme configuration (see footnote 4) would lead to a curve nearly identical with this one.

lower than that expected for linear dependence of magnetic susceptibility on y . In applying figure 2 to the susceptibility measurements made on cow hemoglobin we make the assumption that α has the value 12 for the oxygen equilibrium of this substance; this assumption is a fair one, for measurements of Brown and Hill (3) show that the degree of sigmoid character of the oxygen saturation curve for cow hemoglobin is approximately the same as that for horse hemoglobin.

Titrations of oxyhemoglobin with hydrosulfite

Solutions of oxyhemoglobin were titrated at a room temperature of about 26°C. with standard solutions of sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$). The magnetic susceptibilities for each point during the course of the reduction of oxyhemoglobin to ferrohemoglobin were measured by the Gouy method. (See earlier papers by the authors for descriptions of the method of preparation of cow oxyhemoglobin solutions (12) and of determination of the magnetic susceptibility (11).)

The sodium hydrosulfite solutions were prepared by dissolving about 3 g. of the salt of 85 per cent purity (from the Eastman Kodak Company) and 1.5 g. of anhydrous sodium carbonate in 20 ml. of distilled water. These solutions were kept in a test tube under a thin rubber stopper, and were freshly prepared for use. Small portions of the hydrosulfite were withdrawn in a medical syringe provided with a stainless-steel hollow needle and graduated to 0.01 ml., and were injected through a sliding rubber piston into about 33 ml. of the oxyhemoglobin solution, which was kept without gas phase in the differential susceptibility tube. The tube was rotated end-over-end by motor for 5 min. after each addition of reagent, with glass beads present to aid in stirring. The concentration of the sodium hydrosulfite solution was checked at the beginning and end of each titration by titrating against a pipetted volume of potassium triiodide solution, also under a rubber piston, to the disappearance of the iodine color. From 0.5 to 0.8 ml. of the sodium hydrosulfite solution reduced 20 ml. of the 0.1 N triiodide solution. One oxyhemoglobin titration took from 4 to 7 hr.

Forces in milligrams for a standard magnetic field (Δw) have to be corrected by small quantities for diamagnetism of the reagent added (experimentally determined) and for dilution of the hemoglobin solution, in order to be proportional to the magnetic susceptibilities. There are presented in figure 3 the corrected values of Δw of run No. 1 plotted against the volume of hydrosulfite solution added. A straight line has been drawn through the points taken during the reduction reaction, and this has been continued as a horizontal line after the end point taken at 1.47 ml. Considerations of apparatus and technique lead us to believe that

the error in Δw may amount to ± 0.1 and the error in volume in any addition of hydrosulfite may amount to ± 0.005 ml.

The value of Δw of the initial point differs from zero because the oxyhemoglobin solution is more diamagnetic than water, the experimental reference substance. The average paramagnetic susceptibility of the iron in the solution is proportional to the increase in the corrected Δw over the initial value.

At the beginning of the titration an average of 0.79 ml. of hydrosulfite reduced 20.0 ml. of standard triiodide, and at the end of the titration an average of 0.80 ml. was necessary. It is calculated from these titrations that the effect of decomposition of hydrosulfite on the curve is negligible. Another source of error is the transformation of oxyhemoglobin to ferrihemoglobin at low oxygen pressures (2). Experiments were carried out which showed that this effect caused an increase in Δw of about 0.2 per hour for the middle portion of the curve under the experimental conditions here prevailing. This effect would operate to make the experimental curve slightly concave upwards, but the curvature would be so small as to escape notice. We conclude, therefore, that transformation of oxyhemoglobin to ferrihemoglobin is not a serious source of error in these experiments.

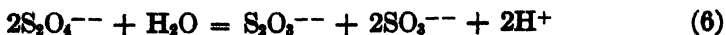
Another oxyhemoglobin solution 0.0133 *f* in heme iron (concentration determined magnetically) was titrated in the same manner, the titration being repeated the next day. The data, corrected for diamagnetism of reagent and dilution, are presented in figure 4. In the first titration, run No. 2, the amounts of hydrosulfite required to reduce 20.0 ml. of triiodide were initially 0.47 and finally 0.50 ml. In run No. 3 the respective titers of the same hydrosulfite solution were 0.53 and 0.57 ml. The magnetic end points came at 0.85 and 1.18 ml. for the two runs, as seen in figure 4.

Before these runs can be interpreted, corrections must be applied for the large change in concentration of hydrosulfite which occurred during the titrations. Meyer (8) has shown that 1 mole of hydrosulfite reduces nearly 1 mole of oxygen to give principally 1 mole of sulfate and 1 mole of sulfite, according to the following equation:



Experiments of Nicloux and Roche (9) include a titration of dog oxyhemoglobin with hydrosulfite with results which correspond to this equation much more closely than do those of Meyer, the better results probably being due to the buffering action of the blood proteins. We can calculate then from an oxyhemoglobin titration the average concentration of hydrosulfite in the reagent.

Meyer also showed (8) that 2 moles of hydrosulfite on decomposition in solution yield 1 mole of thiosulfate and 2 moles of sulfite,



and that the decomposition is catalyzed by the decomposition products. Hydrosulfite, thiosulfate, and sulfite ions reduce respectively 6, 1, and 2 equivalents of triiodide per mole. We calculate from the above information that 3.5 equivalents of reducing power to triiodide disappear per mole of hydrosulfite decomposed. Using the oxyhemoglobin titer and the initial and final triiodide titers, we have calculated accordingly

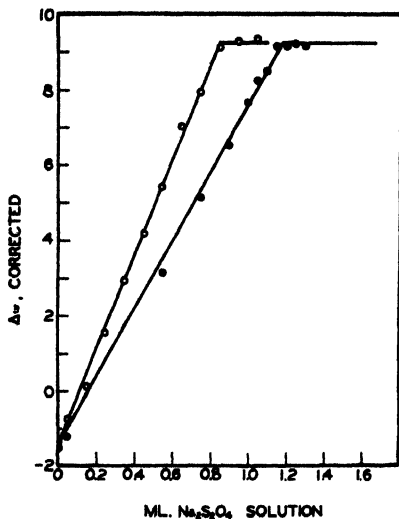


FIG. 4

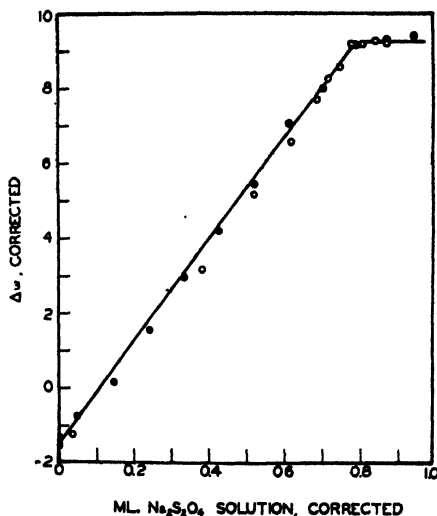


FIG. 5

FIG. 4. Magnetic titrations of oxyhemoglobin solution with sodium hydrosulfite solution. O, run No. 2; ●, run No. 3.

FIG. 5. Magnetic titrations of oxyhemoglobin solution with sodium hydrosulfite solution, with correction for the decomposition of the hydrosulfite. ●, run No. 2; O, run No. 3, with abscissas changed.

that the hydrosulfite concentration decreased 14 per cent during run No. 2 and 19 per cent during run No. 3. The period of time between initial and final titration of the triiodide solution was for each run $5\frac{1}{2}$ hr. Assuming that the rate of decomposition of the solution was essentially constant, we have calculated the concentration of the hydrosulfite solution at the recorded time of each addition, and have expressed the amount added in terms of the volume of the hydrosulfite solution at the concentration prevailing at the start of each run. The end points for the two runs with volume of hydrosulfite expressed in this manner are at 0.79 ml. and 1.10 ml., respectively. We have multiplied the volumes for run No. 3 by the

factor 0.79/1.10 to make them directly comparable with the results of run No. 2, and have presented the runs together in figure 5, with a straight line connecting the initial point and the magnetic end point for comparison with the experimental results.

In a fourth run with a third oxyhemoglobin solution Δw values lie very accurately on a straight line when plotted against volume of hydrosulfite up to three-quarters reduction; during this time very little decomposition of hydrosulfite occurred. At this point the hemoglobin solution was left overnight in the refrigerator, and the titration was continued the next

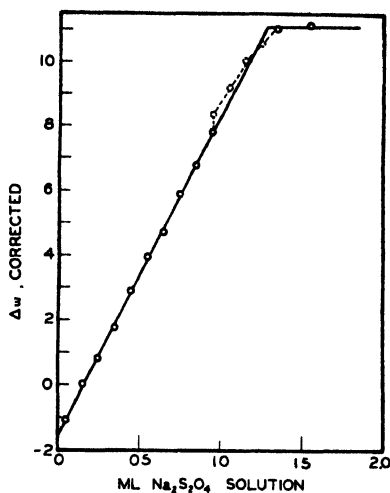


FIG. 6

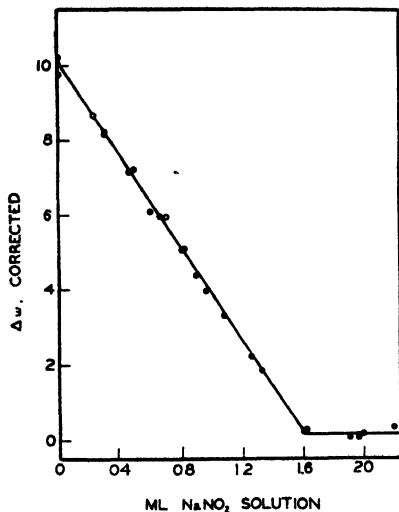


FIG. 7

FIG. 6. Magnetic titration of oxyhemoglobin solution with sodium hydrosulfite solution. Run No. 4. The dashed portion of the curve was obtained the second day.

FIG. 7. Magnetic titrations of hemoglobin solution with sodium nitrite solution at pH 5.5 in the presence of excess hydrosulfite. ○, run No. 11; ●, run No. 12; ◐, run No. 13; ◑, run No. 14.

morning, at which time ferrihemoglobin formation had increased Δw by 0.50 and the hydrosulfite solution had become more dilute. A quantitative determination of the end point in terms of initial oxyhemoglobin and hydrosulfite concentrations cannot be made, but the portion of this run completed the first day gave better linear dependence than any of the three other runs reported, and the extrapolated end point (1.40 ml.) agrees within 0.05 ml. with the end point obtained the next day in the presence of ferrihemoglobin with the then more dilute hydrosulfite solution. The results of this run are presented in figure 6, with broken circles representing the unreliable data of the second day. The straight line representing points of the first day is extrapolated to give the end point.

Conclusions about the oxyhemoglobin-hydrosulfite titrations will be discussed in the third section of this paper.

Titration of ferrohemoglobin with nitric oxide

Solutions of ferrohemoglobin in the presence of hydrosulfite were titrated with a standard solution of sodium nitrite to produce nitric oxide hemoglobin. Ferrihemoglobin solution, used as the source of ferrohemoglobin, was reduced with 0.6–0.9 g. of sodium hydrosulfite. The hemoglobin was retained under a rubber piston, with absence of gas phase, as in the previous experiments with oxyhemoglobin. The concentration of the sodium nitrite solution was determined by oxidation in hot solution with excess standard permanganate and acid, followed by titration with thiosulfate after the addition of iodide. Three titrations gave a mean concentration of 0.353 f.

Meyer (8) found that alkaline hydrosulfite solution does not reduce nitrite and that an excess of hydrosulfite in acid solutions gives nitrous oxide or nitrogen. Nitric oxide is produced in very acid solutions or with an excess of nitrite. Experiments of Coryell and Dodson (5) show, however, that nitric oxide ferrohemoglobin readily forms when hemoglobin is present with hydrosulfite and nitrite, probably because of the high affinity of ferrohemoglobin for nitric oxide and the extreme stability of the compound with respect to reduction. It was also shown that nitric oxide hemoglobin is closely similar in structure to carbon monoxyhemoglobin and oxyhemoglobin in that the iron atoms are involved in octahedral covalent bond formation. There remains, however, one unpaired electron per heme, owing to the odd number of electrons in the NO group. The molal susceptibility of nitric oxide hemoglobin (per heme) was found to be 1280×10^{-6} , that is, about one-tenth of the value for ferrohemoglobin.

Attempts were made to define conditions under which nitrite would be reduced by hydrosulfite in the presence of hemoglobin to give stoichiometric quantities of nitric oxide hemoglobin. Additions of nitrite to hemoglobin-hydrosulfite mixture with bicarbonate-carbonate buffer at pH 9.5 led to only a small reduction in susceptibility even over a period of several days, the average fall in Δw being only 7 per cent of that expected for stoichiometric formation of nitric oxide hemoglobin. Addition of nitrite to hemoglobin-hydrosulfite mixture with acetic acid-acetate buffer at pH of approximately 4.7 led to a large fall of Δw , corresponding to nitric oxide hemoglobin formation, followed by a rise on addition of a second portion. The spectrum then showed the presence of ferrihemoglobin as well as nitric oxide hemoglobin. On longer standing the susceptibility fell and considerable denaturation occurred. It was concluded that titrations at this low pH value could not be carried out because of the rapid destruction of hydrosulfite, leading to slow reduction of nitrite

by other reducing agents, including hemoglobin, and because of the occurrence of denaturation.

It was found that titrations could be made smoothly starting with 35.0 ml. of ferrihemoglobin 0.0147 *f* in heme iron and reduced with at least 0.9 g. of sodium hydrosulfite. The pH of the ferrihemoglobin stock solution was 6.35 (by glass electrode), and the pH during the titration was near 5.5. The titration did not proceed to an end point involving complete formation of nitric oxide hemoglobin when only 0.6 g. of hydrosulfite had been added, but the addition of more hydrosulfite to such solutions with enough nitrite yielded pure nitric oxide hemoglobin (runs 11 and 12). The results of four such runs (11 to 14) are presented in figure 7. Runs 13 and 14 are considered to be more accurate than the others, because the volume of nitrite was computed from the increase in weight of the susceptibility tube and the density of the solution, 1.014 at 25°C., and because they extend over the whole range. Values of Δw have been corrected for dilution of the hemoglobin solution only, since the diamagnetism of the nitrite solution was found not to differ appreciably from that of water.

The end point for the nitrite runs was found to be at 1.595 ± 0.005 ml. for 35.0 ml. of hemoglobin. The end point predicted for stoichiometric reduction of nitrite to nitric oxide is calculated to be at 1.46 ml. This discrepancy of 9.2 per cent arises from reduction of nitrite in part to some substance other than nitric oxide, probably nitrous oxide (8). It is very probable that the fraction of nitrite involved in the subsidiary reaction remains constant during a run.

III. DISCUSSION

The magnetic titrations involving the oxygen-hemoglobin reaction are in definite disagreement with hypothesis I for the structure of ferrohemoglobin, which predicts a pronounced upward concavity of the curve of susceptibility plotted against degree of completion of the reaction. The data presented in figures 3 and 6 show the dependence of susceptibility on degree of oxygenation to be linear to within the experimental error of measurement. The results of figure 5 do not exclude a small upward concavity, but because of the large corrections for progressive change in hydrosulfite concentration these data are much less reliable.

The application of the curve of figure 2 as representative of the predictions of hypothesis I for the nitric oxide hemoglobin reaction cannot be made so directly. The magnetic susceptibility of nitric oxide ferrohemoglobin (5) is incompatible with the existence of complete magnetic interactions for this substance, for this postulate (the analog of hypothesis I for ferrohemoglobin) would require a fraction of a free electron per heme, whereas complete agreement is obtained with the assumption of independent hemes with one free electron apiece. We may, however, proceed

to test hypothesis I for ferrohemoalbumin by making the assumptions that there is complete interaction between ferrohemes but that the nitric oxide ferrohemes are independent of each other and of the ferrohemes, and that the distribution of molecular species is the same for the reaction of hemoglobin with nitric oxide as for that with oxygen (figure 1). The expected susceptibility curve would then be identical with the solid one in figure 2, except for an additional paramagnetism proportional to y to take into account the paramagnetism of the nitric oxide ferrohemes, and would show the same upward concavity. The experimental data given in figure 7 provide the best evidence yet obtained for the linear dependence of susceptibility on degree of reaction. We accordingly reject hypothesis I for ferrohemoalbumin on the basis of this evidence also.

It was assumed in hypothesis II that the ferroheme groups are essentially independent magnetically. It was, however, concluded (12) from consideration of the absolute magnetic moment of the ferrous atom, 5.435, which is higher than expected for ferrous ion by several tenths of a Bohr magneton, that there might be a small amount of magnetic interaction between the ferrohemes associated with the chemical interaction between them. The magnetic titrations, particularly those of the nitrite runs 11 to 14 shown in figure 7, indicate that this interaction has at most only a small effect, for the amount of interaction moment would fall off rapidly as hemes are transformed from the paramagnetic to the diamagnetic state, and upward concavity would be expected for the susceptibility-degree of reaction curve in the manner predicted for hypothesis I, except that the concavity might be much less. We conclude that magnetic interactions between the hemes are not directly detectable at room temperature by titration. Other experimental investigations of possible magnetic interaction effects are under way in these Laboratories.

It has been emphasized previously (12) that the oxygenation of hemoglobin, as well as the reactions with carbon monoxide and with nitric oxide, involve a considerable change in structure, which is reflected in a pronounced change in magnetic properties. The linear dependence of magnetic susceptibility on degree of reaction with substances forming complexes shows that the structure of one heme group (ionic or covalent) does not affect that of another, so far as magnetic properties and bond type are concerned. The bond type of a ferroheme group (Hb) of a hemoglobin molecule is accordingly the same if it is part of the molecule Hb_4 or of a molecule as highly oxygenated as Hb_4O_8 , and the bond type of an oxyheme group (HbO_2) is the same in such diverse molecules as Hb_4O_2 and Hb_4O_8 .

IV. SUMMARY

The theory of chemical interactions between adjacent hemes in hemoglobin has been presented in detail, and the concentrations of various inter-

mediates in the reaction of hemoglobin with oxygen (and probably with carbon monoxide and with nitric oxide) have been calculated as a function of the degree of reaction.

Magnetic measurements have been carried out during titrations involving the transformation of oxyhemoglobin to ferrohemo­globin and of ferrohemo­globin to nitric oxide hemoglobin. From the results of these it is concluded that each of the four hemes of the ferrohemo­globin molecule contains four unpaired electrons (complete ionic structure) and that the magnetic moments of the hemes are essentially independent, the alternative hypothesis of two unpaired electrons per heme with complete magnetic interaction (partially covalent structure) being rejected as incompatible with the experimental data. It is also shown that magnetic titrations at room temperature fail to give evidence of any magnetic effect of chemical interactions between ferrohemes. The magnetic susceptibilities of intermediate compounds formed in hemoglobin reactions are accordingly linearly related to the number of hemes that have undergone reaction.

A quantitative investigation of the reduction of nitrite by hydrosulfite in the presence of hemoglobin to give nitric oxide hemoglobin has been carried out.

REFERENCES

- (1) ADAIR, G. A.: *J. Biol. Chem.* **63**, 529 (1925); *Proc. Roy. Soc. (London)* **A109**, 299 (1925).
- (2) BROOKS, J.: *Proc. Roy. Soc. (London)* **B118**, 560 (1935).
- (3) BROWN, W. E. L., AND HILL, A. V.: *Proc. Roy. Soc. (London)* **B94**, 297 (1923).
- (4) CONANT, J. B., AND MCGREW, R. V.: *J. Biol. Chem.* **85**, 421 (1930).
- (5) CORYELL, C. D., AND DODSON, R. W.: *J. Biol. Chem.*, in press.
- (6) DOUGLAS, C. G., HALDANE, J. B., AND HALDANE, J. S.: *J. Physiol.* **44**, 275 (1913).
- (7) FERRY, R. M., AND GREEN, A. A.: *J. Biol. Chem.* **81**, 175 (1929).
- (8) MEYER, J.: *Z. anorg. Chem.* **34**, 43 (1903).
- (9) NICLOUX, M., AND ROCHE, J.: *Bull. soc. chim. biol.* **8**, 71 (1926).
- (10) PAULING, L.: *Proc. Natl. Acad. Sci. U. S.* **21**, 186 (1935).
- (11) PAULING, L., AND CORYELL, C. D.: *Proc. Natl. Acad. Sci. U. S.* **22**, 159 (1936).
- (12) PAULING, L., AND CORYELL, C. D.: *Proc. Natl. Acad. Sci. U. S.* **22**, 210 (1936).
- (13) TAYLOR, D. S., AND CORYELL, C. D.: *J. Am. Chem. Soc.* **60**, 1177 (1938).

THE EXISTENCE OF CHEMICAL INTERACTIONS BETWEEN THE HEMES IN FERRIHEMOGLOBIN (METHEMOGLOBIN) AND THE RÔLE OF INTERACTIONS IN THE INTERPRETATION OF FERRO-FERRIHEMOGLOBIN ELECTRODE POTENTIAL MEASUREMENTS¹

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INTRODUCTION

In the preceding paper (6) a general application was made of the theory of chemical interactions proposed by Pauling (15) to explain the sigmoid oxygen saturation curve of ferrohemoglobin. It was emphasized there that the chemical interactions between the four hemes, which give rise to a total free energy effect of 6000 cal. per mole, might be detected in different physicochemical studies of hemoglobin systems. Magnetochemical studies (17, 7) have revealed the close analogies existing between the structures of ferrohemoglobin and ferrihemoglobin (methemoglobin) and of some of their compounds. It is the purpose of this investigation to examine all available information about equilibria in ferrihemoglobin systems in order to show that chemical interactions occur also under certain conditions between the hemes of ferrihemoglobin, and to establish the magnitude of their effects in certain equilibria, including the electronic equilibrium with ferrohemoglobin which establishes the electrode potential. These results are of significance to the physical chemistry of ferrihemoglobin and to the structural chemistry of hemoglobin compounds in general.

THE BOND TYPE OF FERRIHEMOGLOBIN COMPOUNDS

The character of the bonds to the iron atom in ferrihemoglobin and in a number of its compounds has been determined in these Laboratories (7). The bonds in ferrihemoglobin were found to be essentially ionic in nature, and the difference between the observed magnetic moment per heme,

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5.80, and the theoretical moment, 5.92,³ was regarded as possibly due to a small amount of magnetic interaction between the ferriheme groups. The addition of diamagnetic alkali fluorides increases the Δw values (forces in milligrams observed in the Gouy apparatus) for ferrihemoglobin solutions through the formation of the more paramagnetic ferrihemoglobin fluoride, for which a magnetic moment per heme of 5.92 was measured, just equal to the theoretical value for the ferric ion. The existence of another form of ferrihemoglobin, ionic in character but with a moment somewhat lower than 5.80, is suggested by the measurements of the magnetic susceptibility of ferrihemoglobin solutions at pH values less than 6.5.

The cyanide and hydrosulfide compounds of ferrihemoglobin, with moments of 2.50 and 2.26, respectively, are essentially covalent⁴ in the character of the six iron bonds (with one odd electron for each ferric atom), and the azide compound was found⁵ also to be covalent in character. It is considered that ferrihemoglobin hydroxide, with a moment of 4.47, has one 3d orbital of the iron atom involved in covalent bond formation, probably with partial covalent character of all iron bonds.

Magnetic titrations of ferrihemoglobin with standard cyanide solution (7) showed linear decrease in susceptibility on adding cyanide at pH values of 6.7 and 10.8. These experiments prove the absence of any strong magnetic interaction in the system of the type discussed for hypothesis I for ferrohemoglobin systems in the paper by Coryell, Pauling, and Dodson (6), but the experiments would not detect small effects due to weak magnetic interactions between the hemes.

THE MATHEMATICAL TREATMENT OF HEMOGLOBIN EQUILIBRIUM DATA

It has been shown (15, 6) that the theory of the existence of chemical interactions in hemoglobin and the assumption of square heme configuration lead to the following equation, connecting the fraction saturation, y , of ferrohemoglobin (assumed not to have heme interactions) with the concentration, c , of a substance forming a compound with heme interac-

³ The magnetic moment of iron group elements is due principally to the spin moments of unpaired electrons in the 3d group. There may be a contribution from the orbital motion of the electrons, which would raise the moment somewhat for elements in the second half of the group. For ferric and manganous ions this contribution will be zero, since the normal state is ${}^6S_{5/2}$; magnetic measurements on inorganic compounds are in agreement with this prediction. There may be a further effect, unpredictable in magnitude and direction, due to magnetic interaction of two or more paramagnetic atoms close together in the molecule.

⁴ The concepts of ionic and covalent bonds and bonds intermediate in type, as well as a discussion of the magnetic criterion for bond type, are clearly presented in *The Nature of the Chemical Bond* (16).

⁵ Unpublished experiments made with Dr. Fred Stitt in these Laboratories.

tions stabilizing the molecule by $RT \ln \alpha$ cal. per mole of adjacent heme pairs:

$$y = \frac{Kc + (2\alpha + 1)K^2c^2 + 3\alpha^2K^3c^3 + \alpha^4K^4c^4}{1 + 4Kc + (4\alpha + 2)K^2c^2 + 4\alpha^2K^3c^3 + \alpha^4K^4c^4} \quad (1)$$

The value of K , the equilibrium constant for addition of the substance to an isolated heme, depends on acidity and temperature. Half-saturation is attained when the product Kc is equal to $1/\alpha$.

It can be shown further that the equation similar to equation 1, derived with the assumption that interactions occur only between adjacent ferrohemes and not between oxyhemes, is identical with equation 1 except for a change in the value of the constant K , whose absolute value has not been determined experimentally. A saturation curve which can be represented by equation 1, with $\alpha \neq 1$, indicates therefore the occurrence of interactions in one or the other, or both, of the pure components of the system. It will be desirable to refer to the interaction constant, α , as the *effective interaction constant*, without for the present designating which of the components has the stabilization free energy. (Indeed, the overall interaction effect may represent a difference of interactions in the pure components from those in the intermediates. It is proposed to discuss this problem at a later time when a greater number of accurate studies have accumulated.) The application of equation 1 to chemical equilibria has so far been the most fruitful method of detecting the presence of and measuring the magnitude of chemical interaction in hemoglobin systems.

It has been customary to represent the sigmoid saturation curves obtained in the study of hemoglobin equilibria by means of an empirical equation proposed by Hill (11):

$$y = \frac{K'c^n}{1 + K'c^n} \quad (2)$$

in which y and c are as defined above and n and K' are empirical constants. We shall use the name *sigmoid coefficient* for n in this equation when applied to experimental studies of hemoglobin equilibria. The value of the sigmoid coefficient is equal to the slope of the line obtained by plotting the logarithm of the ratio of combined to uncombined hemoglobin against the logarithm of the concentration of the combining substance. If equation 1 of this paper is analyzed in this manner with the value of 12 for α , as calculated by Pauling (15) from the horse ferrihemoglobin-oxygen equilibrium measurements of Ferry and Green (9), the value of the sigmoid coefficient is found to be 2.62 for the range of saturation between 10 per cent and 90 per cent, the range most readily accessible for experimental study. Below and above this range it falls to values which approach

unity.⁶ Values of the sigmoid coefficient prevailing in the middle range of saturation have been determined from a logarithmic plot for a number

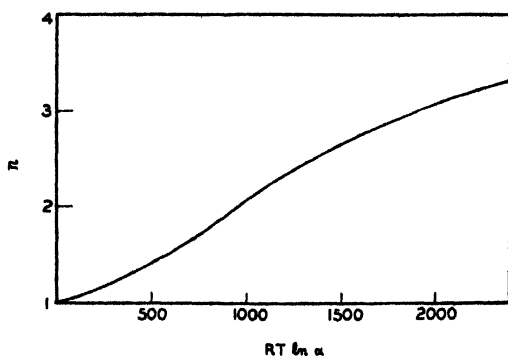


FIG. 1. Sigmoid coefficient n as a function of effective heme-heme interaction energy $RT \ln \alpha$.

of values of α of equation 1, and they have been plotted against $RT \ln \alpha$ in figure 1.⁷ With the help of this curve, values of n reported in the

⁶ The experiments of Ferry and Green (9) give evidence of the smaller slope for very low and very high saturation values, as predicted by equation 1.

⁷ Although equation 2 does not accurately represent the hemoglobin equilibrium, the sigmoid coefficient n may be defined rigorously by the following equation

$$n = \left(\frac{\partial \log R}{\partial \log c} \right)_{R=1} = \left(\frac{\partial \log R}{\partial \log Kc} \right)_{R=1} \quad (3)$$

where R represents the ratio of concentration of hemoglobin complex to that of hemoglobin, $y/(1 - y)$, a function of the variable Kc and the parameter α readily derivable from equation 1. Equation 3 may be modified to give the relation

$$n = \left(\frac{\partial R}{\partial Kc} \cdot \frac{Kc}{R} \right)_{R=1} \quad (4)$$

The term $\partial R / \partial Kc$ is obtained by simple differentiation of the equation for R , and the restrictions of the partial differentiation are fulfilled by setting Kc equal to $1/\alpha$. Collection of terms leads to the following analytic relation between n and α :

$$n = \frac{4\alpha^4 + 28\alpha^3 + 28\alpha^2 + 4\alpha}{\alpha^4 + 12\alpha^3 + 38\alpha^2 + 12\alpha + 1} \quad (5)$$

The value of n calculated from equation 5 using the value of 12 for α is 2.88, which represents the slope of the tangent to the logarithmic curve at the point at which $\log R$ is zero. The value 2.62 derived synthetically, using the same α , is the average value applicable over the range of saturation generally studied in equilibrium measurements. The curve in figure 1 connecting n and α was derived from calculations for the range between 10 and 90 per cent saturation and is therefore to be preferred for empirical use over the curve lying slightly higher that may be calculated from equation 5.

literature for application of Hill's equation may be interpreted directly in terms of heme-heme interaction energy or effective heme-heme interaction constant. For infinite interaction energy the value of the sigmoid coefficient is 4; for zero interaction energy, the values of n and α are unity and equations 1 and 2 reduce to that for the rectangular hyperbola.

We are now in a position to examine the results of certain equilibrium studies reported in the literature. There will first be treated equilibria of ferrihemoglobin with ions involving formation of the covalent hydro-sulfide, azide, and cyanide complexes, then the equilibrium involving formation of the ionic fluoride complex, and finally that involving the partially covalent hydroxide complex. Following this there will be given a discussion of the part played by interactions in an interpretation of the electrode potential studies of hemoglobin.

IONIC-COVALENT FERRIHEMOGLOBIN EQUILIBRIA

Keilin (12) established the fact that hydrogen sulfide reacts with ferrihemoglobin at a pH of approximately 6 to give a reversible complex and determined by a spectrophotometric method a dissociation constant for the complex, assuming independence of the hemes. The values given for the constant show, however, a systematic increase with decrease in hydrogen sulfide concentration at constant pH. I have treated his data anew,⁸ including the results of his Tables I and III as well as those of Table II, from which he determined the simple dissociation constant (1.3×10^{-5} in terms of total uncombined sulfide). The results of this treatment are presented in figure 2, in which $\log \frac{\text{HbSH}}{\text{Hb}^+}$ is given as ordinate with the logarithm of the total uncombined sulfide concentration, $\log (\Sigma \text{H}_2\text{S})$, as abscissa. The points plotted in figure 2 certainly cannot be represented adequately by a line with slope unity, corresponding to the absence of interaction effects. A straight line with slope 1.84 has been fitted to the points; this sigmoid coefficient 1.84 corresponds, as seen from figure 1, to the effective heme-heme interaction energy of 840 cal. per mole or to the interaction constant 4.1.

At pH 6.0 two-thirds of the total sulfide not combined with hemoglobin is in the form of hydrogen sulfide, and one-third is in the form of hydro-sulfide ion, which can combine with hemoglobin (K_a of hydrogen sulfide taken as 3.31×10^{-7} (8)). From figure 2 it is seen that the concentration of total sulfide at which half of the ferrihemoglobin is in complex form is 1.6×10^{-5} , or the concentration of hydrosulfide ion is calculated to be

⁸ Possible effects of the reduction of ferrihemoglobin by hydrogen sulfide (7) have been neglected, as the rate is probably too slow to be observed under the conditions prevailing in these experiments.

5.3×10^{-6} on the assumption that Keilin's solutions were buffered at pH 6.0. Equation 1 accordingly represents the hydrosulfide equilibrium data if α is set at 4.1 and K is set at 4.6×10^4 .

Keilin (13) carried out a less extensive series of experiments, similar to the above, on ferrihemoglobin-azide mixtures, but he did not calculate equilibrium constants from the data. Horse hemoglobin was used, and the pH of the equilibrium experiments was not recorded, although it presumably was approximately 6. Since hydrazoic acid has a dissociation constant of 1.9×10^{-5} , it can be treated as practically completely ionized at pH 6. The data are presented in figure 3, where the abscissas represent

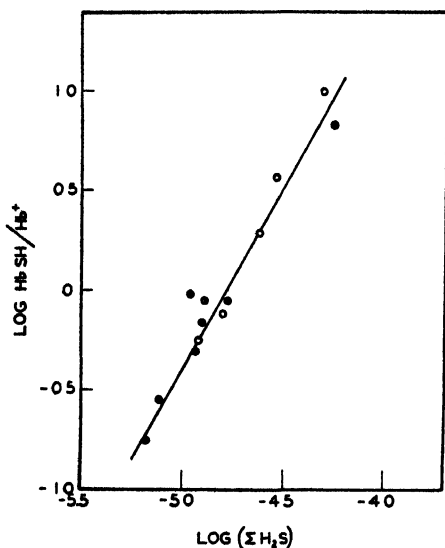


FIG. 2

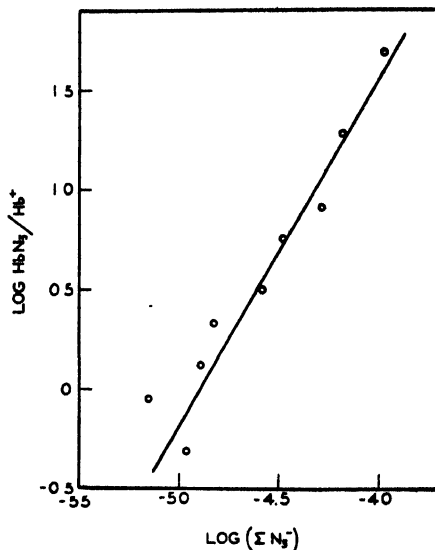


FIG. 3

FIG. 2. Equilibrium between ferrihemoglobin, hydrogen sulfide, and ferrihemoglobin hydrosulfide. Data of Keilin: ●, Table I; ○, Table II; ◐, Table III.

FIG. 3. Equilibrium between ferrihemoglobin, azide ion, and ferrihemoglobin azide.

the logarithm of the total concentration of azide not combined with hemoglobin. A straight line of slope 1.76 has been fitted to the points as a reasonable representation, corresponding (figure 1) to a heme-heme interaction energy of 780 cal. per mole or an effective interaction constant of 3.7. The azide concentration at half-saturation is 1.3×10^{-5} , leading to the value 2.1×10^4 for K in equation 1.

For these two reactions values of the effective interaction energy are, respectively, 840 and 780 cal. per mole of adjacent heme pairs. These figures are based on the assumption of square heme configuration, but the values per molecule (3360 and 3120 cal.) are essentially independent of the structural configuration assumed (15). Considering the relatively large

experimental uncertainty (of the order of magnitude of 10 per cent) in the determination of these two effective interaction energies, it might be concluded that the interaction constants are really identical to within experimental error for these two ionic-covalent equilibria. The possibility that the corresponding ionic-covalent equilibria of ferrohemoglobin with oxygen and with carbon monoxide have identical interaction constants has already been discussed (6). Final conclusions about the identity of effective interaction constants for different reactions must await the execution of more accurate investigations.

The equilibrium between ferrihemoglobin and hydrocyanic acid was studied magnetometrically by Coryell, Stitt, and Pauling (7) at pH 4.77. The results, presented in figure 3 of their paper, are represented by a theoretical curve calculated for equilibrium with independent hemes. The author has reexamined their original data, and has found that the measurements are not sufficiently accurate to prove the presence or the absence of interaction effects, or to eliminate the possibility of an interaction constant as large as 4.

EQUILIBRIA WITH PREDOMINANT IONIC CHARACTER IN BOTH COMPONENTS

Ferrihemoglobin readily forms ferrihemoglobin fluoride, and in both compounds the iron atom is held by essentially ionic forces. No analogous system has yet been found with ferrohemoglobin, so it is interesting to determine whether the effect of interactions is observable in these equilibrium data. Lipmann (14) has made a spectrophotometric study of the equilibrium, using swine ferrihemoglobin at pH 6.9. His data are analyzed for the sigmoid coefficient in figure 4. The greatest significance is to be attached to the experiments made with comparable concentrations of the two compounds, in the middle range of the plot, and through these points has been drawn a line with slope unity, which crosses the zero ordinate at an abscissa corresponding to the simple dissociation constant of 0.0138 given by Lipmann. It is concluded from these experiments that the effective interaction constant for the equilibrium is 1.00; the corresponding value of K for equation 1 is 72.5, the reciprocal of the dissociation constant.

As discussed in the second section of this paper, it is believed that iron atoms in ferrihemoglobin hydroxide are held by bonds which are only partly covalent, and therefore partially ionic, in nature. Extensive experiments on the ferrihemoglobin-ferrihemoglobin hydroxide equilibrium have been made spectrophotometrically by Austin and Drabkin (1) and magnetometrically by Coryell, Stitt, and Pauling (7). The data of both sets of workers have been published, with curves showing the equilibrium as a function of pH, assuming the absence of interaction effects. There are presented in figure 5 data of the latter set of workers analyzed for the

sigmoid coefficient, using all of the data in the pH range 7.3 to 9.1 from their Table I (7). A straight line of slope unity has been fitted to the points; the data of Austin and Drabkin would give the same slope with equal certainty. We conclude, therefore, that the effective interaction constant is 1.00 for this equilibrium. The value of K for equation 1 is 7.1×10^5 for this series of measurements.

There are two possible explanations of the observation of effective interaction constants of unity in ionic hemoglobin equilibria. It is possible, first, that no interactions exist between the hemes of either component, or, second, that the effect of ferriheme-ferriheme fluoride interactions, for

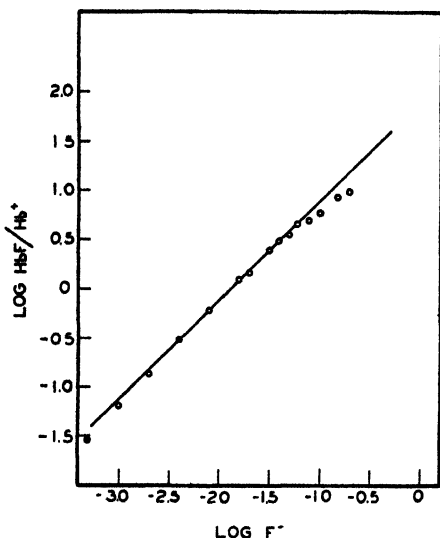


FIG. 4

FIG. 4. Equilibrium between ferrihemoglobin, fluoride ion, and ferrihemoglobin fluoride.

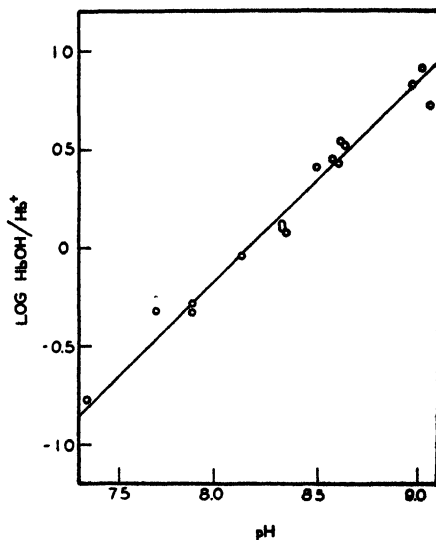


FIG. 5

FIG. 5. Equilibrium between ferrihemoglobin and ferrihemoglobin hydroxide as a function of pH.

example, cancels exactly the effect of ferriheme-ferriheme and ferriheme fluoride-ferriheme fluoride interactions. Evidence to be brought forward in the next section gives indication of the existence of interactions in ionic hemoglobin compounds and therefore supports the second possibility, but more quantitative information about the absolute magnitudes of the interaction effects has not yet been obtained.

THE FERRO-FERRIHEMOGLOBIN ELECTRODE POTENTIAL

It was shown by Conant (2) that the oxidation of ferrohemoglobin to ferrihemoglobin involves one equivalent per heme group. The electrode reaction for the ferro-ferrihemoglobin half-cell, symbolically written,



represents an equilibrium between electrons (E^-), ferrihemes (Hb^+) of ferrihemoglobin, and ferrohemes (Hb) of ferrohemoglobin. The concentration of electrons, at 25°C ., in terms of those in the reference half-cell is given by the following expression

$$\log (\text{E}^-) = -\frac{E_{\text{obsd.}}}{0.059} \quad (7)$$

We expect therefore that the electrode potential of hemoglobin, represented by equation 6, should be in accord with the general hemoglobin equilibrium equation (equation 1).

A determination of the slope of the curve representing $\log \frac{(\text{Hb})}{(\text{Hb}^+)}$ as ordinates plotted against $-\frac{E_{\text{obsd.}}}{0.059}$ as abscissas gives the value of n of the Nernst equation which is in agreement with the measurements. By virtue of equation 7, however, the n of the Nernst equation is identical with the sigmoid coefficient for reaction 6. We can therefore make use of reported values of n in the Nernst equation and figure 1 to obtain information about the effective interaction constant for equation 1. The representation of the half-cell reaction as a typical hemoglobin equilibrium offers an explanation for the occurrence of values for n in the Nernst equation greater than unity for an oxidation involving a change in valence of unity for the iron atoms.

The ferro-ferrihemoglobin electrode potential has been studied potentiometrically by Conant and coworkers (2, 3, 4) and by Havemann and Wolff (10) and spectrophotometrically in oxidation equilibria by Conant and Scott (5). There are numerous difficulties in the measurement of the potential, and consequently measurements of the sigmoid coefficient are subject to some uncertainty. There are presented in table 1 values of the sigmoid coefficient for the oxidation reaction from all available experiments in the literature with sufficient data for the calculation to be made. All experiments except one at pH 7.7 have been made with horse hemoglobin. Conant and Scott (5) and Conant and Pappenheimer (4) have carried out the only experiments specifically devised to determine n ; some of the other calculations of n rest on comparatively few measurements with large experimental error.⁹

The potentiometric measurements give values of the sigmoid coefficient between 1.2 and 1.7, without clear evidence for any dependence on pH.

⁹ Note added in proof: Dr. John F. Taylor (private communication) has recently carried out measurements of the electrode potential in which a high degree of reproducibility was attained. He reports that n of the Nernst equation is greater than unity but seems to depend somewhat on the fraction of hemoglobin oxidized.

The transformation of ferrihemoglobin to the hydroxide is half effected at pH 8.2 (figure 5); studies in solutions much more alkaline than this involve the reduction of ferrihemoglobin hydroxide to ferrohemoglobin. The two spectrophotometric studies (5), in which the equilibrium was

TABLE 1
Sigmoid coefficient for the ferro-ferrihemoglobin electrode potential

pH	METHOD OF STUDY	REFERENCE	n^*	DISCUSSION OF DATA
6.4	E.M.F. of mixtures	(3)	1.4	Best series in paper. Three concentration ratios in duplicate
6.9	Spectrophotometric. 1-Naphthol-2-sulfonate indophenol. Equilibrium	(5)	2.0 ± 0.5	Sixteen experiments (figure 3)
6.9	Spectrophotometric. Ferricyanide-Hb equilibrium in presence of carbon monoxide	(5)	2.0 ± 0.3	Thirteen experiments (figure 4)
7.0	E.M.F. of mixtures. $\text{Fe}(\text{CN})_6^{---}$ catalyst	(4)	1.35	Data of figure 1, reinterpreted to give smaller average deviation (1.23 given by authors). Nine concentration ratios, best series in paper
7.0	E.M.F. of mixtures	(4)	1.0-2	Reported results of other series (no data given)
7.7	E.M.F. $\text{Fe}(\text{CN})_6^{---}$ titration curves	(10)	1.2	Interpretation of titration curve, figure 2. Three points, cow hemoglobin
8.4	E.M.F. of mixtures	(3)		Data not self-consistent
8.5	E.M.F. $\text{Fe}(\text{CN})_6^{---}$ titration curve	(2)	1.4	Data of Table II. Nine points
8.5	E.M.F. $\text{S}_2\text{O}_4^{--}$ titration curve	(2)	1.2	Data of Table II; assumed starting point at -4.0 ml. Ten points
9.5	E.M.F. of mixtures	(3)	1.7	Data not very consistent. Three concentration ratios in duplicate

* The value of the sigmoid coefficient n is also the experimental value of n from the application of the Nernst equation to the results.

approached from both sides, give much higher values, approximately 2.0. It seems to be definitely shown by the evidence given in table 1, however, that the sigmoid coefficient is greater than unity. Values of 1.2, 1.6, or 2.0 (covering the range of values found in table 1) correspond respectively

to values of 1500, 2600, or 3800 cal. total effective interaction energy per mole, or to values of 1.9, 3.0, or 5.0 for the effective interaction constant. It is thus seen that interaction effects play an important part in the oxidation of hemoglobin.

It was mentioned in connection with equation 1 that the effective interaction may be a function of various interactions between like and unlike adjacent hemes. The occurrence of interaction effects in the ferro-ferrihemoglobin-electron equilibrium does indicate, however, that ionic compounds have stabilizing interactions, and that the non-observance of interactions in the ferrihemoglobin-fluoride and ferrihemoglobin-hydroxide systems is probably due to a cancellation of interaction effects, rather than to their non-existence.

SUMMARY

Analyses of the equilibrium data for the reactions between ferrihemoglobin and hydrosulfide and azide ions lead to the conclusion that stabilizing heme-heme interactions occur in these systems analogous to those occurring in the ferrohemoglobin system with oxygen.

A method is presented by which the empirical n of Hill's equation for hemoglobin saturation equilibria (the sigmoid coefficient) can be correlated with the corresponding value of α (the effective interaction constant) for Pauling's theoretical treatment of chemical interactions between adjacent hemes.

The values of the total effective interaction energies ($4RT \ln \alpha$) for four equilibria have been ascertained. The experimental values in calories per mole are 3360, 3120, 0, and 0, respectively, for the equilibria with hydrosulfide, azide, fluoride, and hydroxide ions. In the first two equilibria, complexes with covalent ferric atoms are formed; in the last two, complexes with predominantly ionic ferric atoms are formed.

The ferro-ferrihemoglobin half-cell has been treated as an equilibrium between these two substances and electrons. This treatment leads to the conclusion that the n of the Nernst equation applied to these potential measurements is identical with the sigmoid coefficient, and explains the occurrence of values of n greater than unity for a one-step oxidation of iron atoms. The fact that n is in the neighborhood of 1.6 indicates that interactions occur in this system of hemoglobin compounds, both of which contain ionically bound iron, and that an interaction energy effect of approximately 2600 cal. per mole is involved.

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REFERENCES

- (1) AUSTIN, J. H., AND DRABKIN, D. L.: *J. Biol. Chem.* **112**, 67 (1935).
- (2) CONANT, J. B.: *J. Biol. Chem.* **57**, 401 (1923).
- (3) CONANT, J. B., AND FIESER, L. F.: *J. Biol. Chem.* **62**, 595 (1925).
- (4) CONANT, J. B., AND PAPPENHEIMER, A. M.: *J. Biol. Chem.* **98**, 57 (1932).
- (5) CONANT, J. B., AND SCOTT, N. D.: *J. Biol. Chem.* **79**, 207 (1928).
- (6) CORYELL, C. D., PAULING, L., AND DODSON, R. W.: *J. Phys. Chem.* **43**, 825 (1939).
- (7) CORYELL, C. D., STITT, F., AND PAULING, L.: *J. Am. Chem. Soc.* **59**, 633 (1937).
- (8) EFFRECHT, A. G.: *Helv. Chim. Acta* **21**, 208 (1938).
- (9) FERRY, R. M., AND GREEN, A. A.: *J. Biol. Chem.* **81**, 175 (1929).
- (10) HAVEMANN, R., AND WOLFF, R.: *Biochem. Z.* **293**, 399 (1937).
- (11) HILL, A. V.: *Biochem. J.* **7**, 471 (1913).
- (12) KEILIN, D.: *Proc. Roy. Soc. (London)* **B113**, 393 (1933).
- (13) KEILIN, D.: *Proc. Roy. Soc. (London)* **B121**, 165 (1936).
- (14) LIPMANN, F.: *Biochem. Z.* **206**, 171 (1929).
- (15) PAULING, L.: *Proc. Natl. Acad. Sci. U. S.* **21**, 186 (1935).
- (16) PAULING, L.: *The Nature of the Chemical Bond*. Cornell University Press, Ithaca, New York (1939).
- (17) PAULING, L., AND CORYELL, C. D.: *Proc. Natl. Acad. Sci. U. S.* **22**, 210 (1936).

THE FLOW OF CREAM THROUGH NARROW GLASS TUBES

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The flow properties of milk, cream, and ice-cream mixes have been comparatively little studied. Bateman and Sharp (2) showed that, for ice-cream mixes over a limited range of stress, the rate of flow was linearly related, but not proportional, to the shearing stress; in another paper (3) they showed that the viscosity of various kinds of milk fell with increasing stress, and also that the viscosity, reduced by shearing, rose again on resting the sample. This last phenomenon ("false body") they ascribed to changes in the conditions of the fat clumps. These authors worked at 25°C., and they suggested that the fall in viscosity produced by shearing is more marked at low than at high temperatures.

Mohr and Oldenburg (13) made a very thorough rheological study of milk and cream, using consistometers of various types (rotating cylinder, capillary, and falling cylinder). To interpret their data they used an equation of the Ostwald-de Waele type, in which the logarithm of the shearing stress is plotted against the logarithm of the rate of shear. Over a certain limited stress range, curves obtained in this way are linear, but the range of stresses used was so wide that many of the data fell outside the linear part of the curve.² Mohr and Oldenburg also investigated the viscosity-concentration relation, which has recently received a very interesting treatment at the hands of Leighton and his coworkers (8, 9, 10, 11, 12), but this problem is not discussed in the present paper. In some of Leighton's papers, however, the authors do claim a linear relation between flow rate and shearing stress. A certain amount of other work has been done (20), but it was felt that the whole question of the nature of the flow of cream and milk through narrow tubes required further investigation, and that the results of such an investigation might well lead to methods of measuring the physical properties of these systems which would be of commercial importance.

For this purpose a capillary consistometer of the type known as the

¹ New York State Agricultural Experiment Station, Geneva, New York. This article was approved by the Director as Journal Paper No. 341.

² For a full account of the rather complex rheology of these systems see reference 18, page 70.

Rothamsted plastometer was used. This instrument, which is a modification of the Bingham plastometer, has been fully described in the literature (19, 17). It is sufficient here to say that in this instrument the material is forced by compressed air at known pressure through a series of standardized glass capillary tubes, the ends of which are connected to pipets. When one pipet is emptied the direction of shear can be reversed, so that the material can be sheared back and forth as often as is desired. The air displaced by the cream flowing into the initially empty pipet is allowed to escape through a series of capillary tubes whose resistance is known and can be varied, and, since air is a true fluid, the rate of escape of air, and hence of the flow of the cream, is proportional to the pressure at the entrance to the leak, which is measured on a sensitive manometer. It is found that for cream and milk a slight progressive breakdown occurs during the process of shearing unless the temperature is such that the fat globules are liquid. For this reason a temperature of 37°C. was used for the present work. This also has the advantage of being the temperature at which milk is actually drawn from the cow. Under these conditions, neglecting the first shear in which "false body" is destroyed and correcting for certain minor irregularities, it is found that repeated shearing gives reproducible data for milk, natural cream, and such artificial creams as are sufficiently stable to be worth investigating.

Because of the irregularities of the first shear, it is not possible to study the amount (if any) of the breakdown produced by shearing by a direct method, but, if a general relation can be assumed between S (shearing stress), V (flow in cubic centimeters per second), R (radius), and L (length), then, since the amount of breakdown will depend on R and L , deviations from the simple relation when these factors are varied will indicate the extent of the breakdown. It will be shown later that not only breakdown, but in certain cases the building up of structure as a result of shear, have to be considered. Schofield and Scott Blair (15) have shown³ that, whatever assumption is made about the relationship between velocity gradient and stress in anomalous systems, curves⁴ (hereinafter called "flow curves") obtained by plotting $V/\pi R^3$ against $PR/2L$ (shearing stress at wall) must be unique, i.e., independent of R and L so long as the following three criteria remain true: (a) Each particle of the material moves in a straight line, at a constant velocity, parallel to the axis of the tube. (b) There is no slip at the wall. (c) The velocity gradient, at any point, is some function of the shearing stress at that point, and depends on nothing else.

Quite apart from the case of simple plug flow at stresses below the yield value, divergences have been observed for a number of materials.

³ Similar ideas were developed at almost the same date by a number of authors. The question of priority is somewhat involved (see reference 18, page 37).

⁴ P must, of course, be expressed in dynes per square centimeter.

In some cases these divergences are due to a breakdown of the material, thus invalidating condition c , and such breakdown may be irreversible or reversible, the latter being a manifestation of false body. Ambrose and Loomis (1) studied materials (bentonites) which show false body,⁵ but Schofield and Scott Blair (15) showed that in the case of many clays and certain other materials some mechanism other than a breakdown is at work, since with these materials the position of the flow curve is affected by changes in R but not in L , whereas any type of breakdown under shear would be more marked the greater the value of L .

Philippoff (14) has recently studied a large number of materials many of which show divergence; in some cases these are caused by false body, whereas in others they are caused by anomalous flow near the wall of the tube.

The Rothamsted plastometer has been in use for a number of years for work with clays, soils, and the like, and has shown itself convenient to operate, especially on account of the speed with which results can be obtained, no weighings or time readings being needed once the instrument has been standardized. Its usefulness for cream was at first questioned on account of a phenomenon which has not yet been fully explained. Neglecting the first shear, although the second shear gives consistent data, by about the third, fourth, or fifth shear it is found that, while the pressure is held constant, the flow is at first rapid, and then gradually falls during the shear. On reversing the direction of shear and using the same pressure, the flow rate again starts high and falls during the shear. This phenomenon becomes worse as the experiment proceeds. Fortunately, it can be entirely eliminated by stirring the cream thoroughly between the shears. This is easily effected by allowing a few bubbles of air to pass along the capillary and so up through the cream in the full pipet. The phenomenon is presumably caused by some kind of packing effect, though it can be shown that this does not take place primarily in or at the entrances of the capillary, since air introduced through a side tube and bubbled through the bulk of the cream, but not through the capillary, is effective in eliminating the trouble.

A large number of creams,—natural, homogenized, and reconstituted from milk and butter with and without stabilizers,—have been tested. The results show (1) excellent reproducibility in almost all cases and (2) extremely complex rheological conditions. It was hoped that the great variety in rheological properties met with might enable different types of cream, indistinguishable by chemical means, to be recognized. Generally speaking, it has not yet been possible to do much along these lines, though

⁵ The term "thixotropy" is used. Strictly speaking, this should refer only to a true gel-sol transformation, hence the term "false body" is preferred. Time alone will show whether the distinction is worth preserving.

it is hoped that further work may lead to some such practical use for the method. It is clear that nothing of this kind will be possible until the flow properties of cream have been fully investigated. It was found that many natural and a few reconstituted creams, of both high and low viscosity, show straight-line flow curves passing through the origin, and in many cases these are "unique" (i.e., independent of variations in R and L). These systems are true fluids and will be classed as α . Others (β) show unique curvilinear flow curves; others (γ) again show straight-line curves which diverge; and others (δ) show curvilinearity and divergence. In all cases of curvilinearity, the logarithmic flow curves (plotting $\log(V/\pi R^3)$ against $\log(PR/2L)$) are linear over a considerable range. In most cases the exponent (which we shall call n)⁶ is greater than 1, i.e., viscosity falls with rising stress (cases $\beta 1$ and $\delta 1$), and the system shows "structural viscosity" in the Ostwald sense, but in a few rare cases values of n of less than 1 have been obtained ($\beta 2$ and $\delta 2$). This phenomenon may be analogous to the "inverse thixotropy" of certain emulsions and other colloidal systems (5, 6, 7). It must be remembered that the phenomenon of thixotropy or false body can be distinguished from this type of structural viscosity (fall in viscosity with rising stress) only when the rate of recovery is comparatively slow. Systems $\beta 2$ and $\delta 2$ may be, in a sense, dilatant (4) or may be regarded as exhibiting a type of strain-hardening. One of us (J.C.H.) has observed that in using a McMichael viscometer with thick cream, the viscosity increased with the shearing. This is probably the same phenomenon.

Rare but authentic cases have been observed where the divergence of the flow curve is in the opposite sense from the normal. When breakdown occurs, the viscosity is naturally less in the narrower and longer tubes, but in these rare cases (which may be classed as ϵ) the reverse is the case, viscosity being greatest in the widest and shortest tubes. This is doubtless another manifestation of the same kind of phenomenon.

It must be emphasized that there is no direct relation between viscosity, divergence, and curvilinearity. Some creams of high viscosity are truly fluid, while other thinner creams show either or both of the anomalies at the temperature at which the experiments were done. It will, however, be shown later that the same cream, diluted so as to vary its viscosity, tends to vary its divergence in a regular way. Various authors have attempted to relate the viscosity of cream to its microscopic structure. Before discussing our experiments on the microscopic structure, it would be well to consider the question of viscosity. It is clear that some criterion of viscosity must be established if figures are to be obtained to correlate with the microscopy data. For true fluids (α), the evaluation is simple.

⁶ $n = d[\log(V/\pi R^3)]/d[\log(PR/2L)]$.

In accordance with the Poiseuille-Hagen law, we have for viscosity, η ,

$$\eta = \frac{1}{4} \left(\frac{PR}{2L} / \frac{V}{\pi R^3} \right)$$

so that viscosity is given directly by the slope of the flow curve.

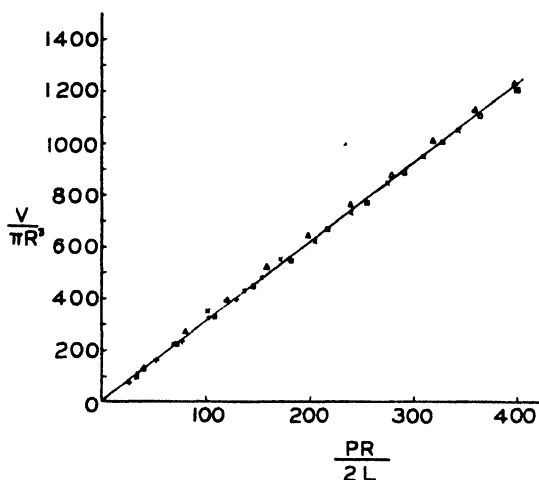


FIG. 1. Typical flow curve for creams of the α -type. \times , capillary II, $R = 0.0258$ cm., $L = 19.9$ cm.; \triangle , capillary III, $R = 0.0302$ cm., $L = 20.0$ cm.; \square , capillary IV, $R = 0.0550$ cm., $L = 20.0$ cm.; $+$, capillary V, $R = 0.0773$ cm., $L = 19.8$ cm.

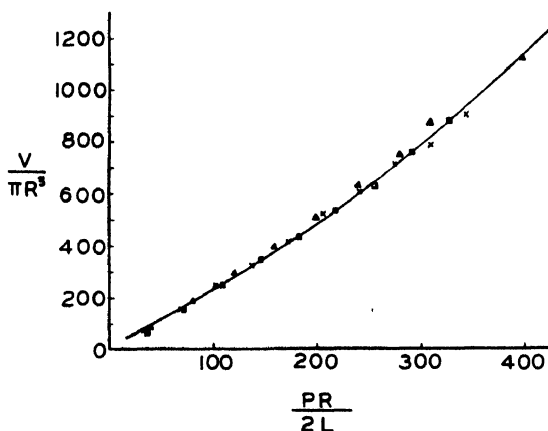


FIG. 2. Typical flow curve for creams of the β -type. \times , capillary II, $R = 0.0258$ cm., $L = 19.9$ cm.; \triangle , capillary III, $R = 0.0302$ cm., $L = 20.0$ cm.; \square , capillary IV, $R = 0.0550$ cm., $L = 20.0$ cm.

There arises the problem of what is to be done for systems which are not truly fluid. The whole question has been discussed in connection with

curvilinearity for such systems as flour doughs by Schofield and Scott Blair (16) and by the same authors for cases of divergence in the papers already quoted (15).

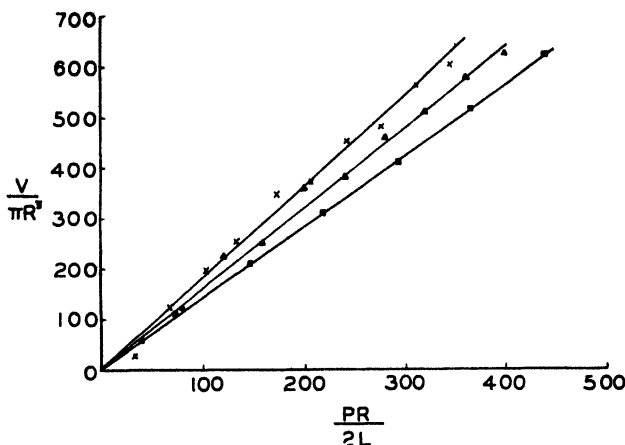


FIG. 3. Flow curves for creams of the γ -type. \times , capillary II, $R = 0.0258$ cm., $L = 19.9$ cm.; Δ , capillary III, $R = 0.0302$ cm., $L = 20.0$ cm.; \square , capillary IV, $R = 0.0550$ cm., $L = 20.0$ cm.

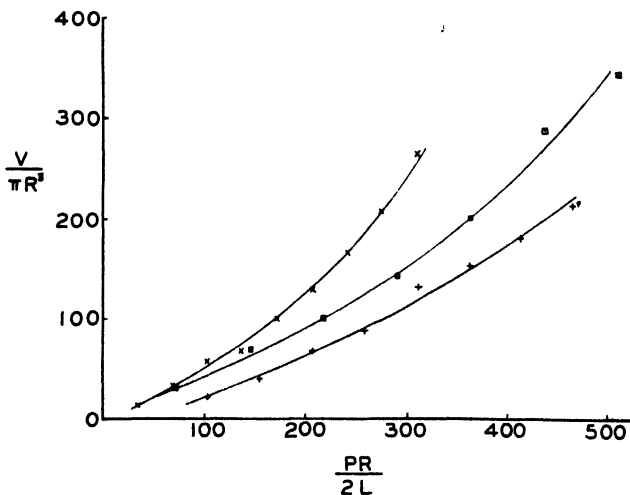


FIG. 4. Flow curves for creams of the δ -type. \times , capillary II, $R = 0.0258$ cm., $L = 19.9$ cm.; \square , capillary IV, $R = 0.0558$ cm., $L = 20.0$ cm.; $+$, capillary V, $R = 0.0773$ cm., $L = 19.8$ cm.

Some authors believe that it is inadvisable to report viscosities in c.g.s. units unless these viscosities are independent of stress and of the dimensions of the apparatus. We cannot agree with this point of view since,

to be logical, the same argument should be applied to variations with changes in temperature, in which case no viscosities could be quoted at all. If viscosities are to be reported for arbitrary temperature, stress, and conditions of shear, these factors must, of course, be clearly stated, and for

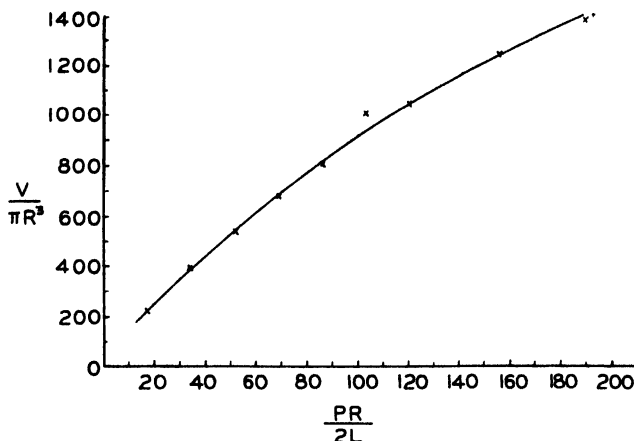


FIG. 5. Flow curve for a cream of the β_2 -type ($n < 1$). \times , capillary II, $R = 0.0258$ cm., $L = 19.9$ cm.

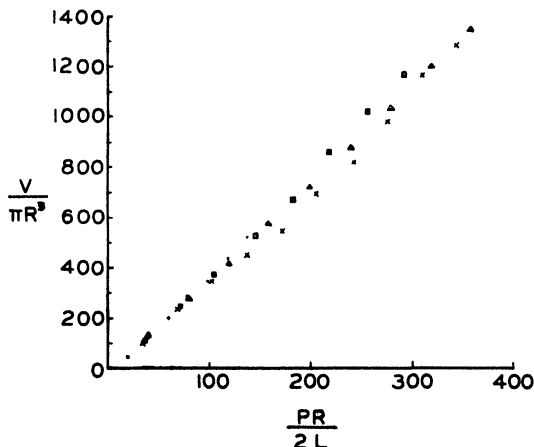


FIG. 6. Results obtained with a cream of the α -type. \times , capillary II, $R = 0.0258$ cm., $L = 19.9$ cm.; \triangle , capillary III, $R = 0.0302$ cm., $L = 20.0$ cm.; \square , capillary IV, $R = 0.0550$ cm., $L = 20.0$ cm.; \bullet , capillary IVa, $R = 0.0554$ cm., $L = 73.7$ cm.

different materials different data will be required. For cream it is necessary to state the temperature (in our case $37^\circ\text{C}.$), the shearing stress (for non-fluid systems an arbitrary value of 200 dynes per square centimeter is chosen), and the radius and length of the tube. For reproducibility, the

pretreatment of the sample must of course be controlled. These viscosities are, of course, an arbitrary criterion, but it is found that, in conjunction with n and the amount of divergence, they form useful practical criteria for cream; moreover, obtaining the whole series of flow curves gives far more information than any single viscosity determination such as could be obtained in an ordinary viscometer.

In figures 1 and 2 are shown typical flow curves for creams of types α and β ; in figure 3 curves for type γ ; in figure 4 curves for type δ . Figure 5 shows a case of $n < 1$ (type $\beta 2$), and figure 6 a case where the divergence is inverted (type ϵ).

TABLE 1
Values obtained with different capillaries

SAMPLE	CAPILLARY II		CAPILLARY III		CAPILLARY IV		CAPILLARY IVA	
	η	n	η	n	η	n	η	n
1	0.287	1.13	0.405	1.51	0.405	1.21	0.405	1.04
2	0.137	0.97	0.158	0.97	0.177	1.00	0.161	1.00
3	0.158	0.93	0.189	1.05	0.198	1.02	0.189	1.07
4	0.106	0.90	0.109	0.92	0.114	0.92	0.095	1.00
<i>R</i>	0.0258		0.0302		0.0550		0.0554	
<i>L</i>	19.9		20.0		20.0		23.7	

Effect of capillary II on size of globules and clumps

SAMPLE	AVERAGE SIZE OF GLOBULES (μ)		AVERAGE SIZE OF CLUMPS (μ)	
	Before shear	After shear	Before shear	After shear
1	2.37	2.37	4.78×6.75	4.51×6.31
2	1.78	1.82	4.24×2.90	4.40×2.98
3	1.38		3.71×2.72	
4	1.28	1.42	2.90×2.12	2.75×1.98

MICROSCOPIC TECHNIQUE

The fat globules and fat globule clumps were measured at a magnification of approximately 1300 diameters, using an ocular micrometer disc standardized with the microscope so adjusted that each of the smallest divisions represented 1 micron. Three-tenths of a cubic centimeter of the cream to be examined was diluted with 100 cc. of water and mounted as a hanging drop preparation. Two hundred fat globules and the clumps found in the fields were measured for each cream, except in some cases in which the number of clumps exceeded the number of globules and the procedure was reversed.

In order to illustrate the sort of data that were obtained by this tech-

nique, an experiment will be described in which it was intended to find out whether shearing through the narrowest capillary used, capillary II, ($R = 0.0258$ cm., $L = 19.9$ cm.) would affect the size of globules and clumps. A sample of reconstituted cream was made by passing the usual mixture of butter and milk once through a household emulsifier (sample 1; fat about 30 per cent). The remainder of sample 1 not used in the test was again passed through the emulsifier, and a second sample taken for testing (sample 2). The same procedure was repeated for a third sample (sample 3) and again for a fourth, except that in this last case the screw of the emulsifier was loosened slightly. These four samples were tested with capillary II, and examined microscopically before and after the test. The results are given in table 1.

The microscopic examination was made only in the case of capillary II, but it is clear that shearing, which has produced definite divergence, has not shown any significant effect on the size either of the globules or of the clumps. The usual relationship between the size of fat globule clumps and

TABLE 2
Effects of pressure used in emulsification and of egg yolk

SAMPLE	FIRST TEST		SECOND TEST (AFTER 24 HR. IN REFRIGERATOR)	
	η	n	η	n
1	0.07	1.00	0.07	0.93
2	0.08	1.00	0.08	0.97
3	0.07	1.07	0.07	1.07
4	0.08	1.04	0.08	1.02

the viscosity of homogenized and reconstituted creams was demonstrated in these experiments. A number of workers have shown that increases in the size of fat globule clumps produced by homogenizing natural or reconstituted creams and ice-cream mixes increased their viscosity. The effects of the pressure used in emulsification and of egg yolk are shown in table 2.

The reconstituted creams⁷ containing 30 per cent milk fat were numbered as follows:

Sample 1: No egg yolk; homogenized at 1000 pounds per square inch

Sample 2: No egg yolk; homogenized at 2000 pounds per square inch

Sample 3: + 2.5 per cent egg yolk; homogenized at 1000 pounds per square inch

Sample 4: + 2.5 per cent egg yolk; homogenized at 2000 pounds per square inch

⁷ We are indebted to the Staff of the Laboratories of Messrs. J. Lyons and Co., Ltd., for their kindness in preparing these samples especially for our experiments.

The butter and milk mixtures used for the experiment reported in table 2 were heated to 65.5°C. (150°F.), and each mixture was passed twice through the homogenizer at the pressure stated and then at a lower pressure (approximately 200 pounds per square inch). The products were finally cooled by passing over a small cooling screen.

Table 2 shows that it is possible to make reconstituted creams which are true fluids, showing neither divergence nor curvilinearity, both with and without egg yolk. The egg yolk did not affect viscosity, but the cream prepared at the higher pressure had in all cases a slightly higher viscosity.

It was originally intended to study the effects produced by a temperature treatment for increasing the consistency of sweet cream as described by Hening and Dahlberg (6a). Most of the increased consistency is lost when the cream is warmed to 37°C. for the test. Comparatively few British houses have refrigerators of any kind and larders are often far from cool, so that conditions are different from those in the United States, where an increased consistency need not withstand anything but comparatively low temperatures. For this reason, the problems concerning consistency induced by cooling have not been investigated.

The effect of concentration on the divergence of flow curves has been studied by Schofield and Scott Blair (15) in the case of clays, and it was found that the effect is greatest at a moderate concentration and less in high and low concentrations. It must be remembered that this phenomenon is not a breakdown such as is found in cream, and it is of interest to enquire as to the effect of varying the fat content on the divergence of the flow curves.

A number of experiments have been done on natural creams, all of which go to show that the higher fat content tends to give an inverted or negligible divergence, whereas the lower fat content gives a higher divergence.

SUMMARY

1. Creams,—natural, homogenized, and reconstituted,—have been sheared through glass capillary tubes under pressure at a temperature of 37°C., and flow curves plotting the rate of shear against shearing stress have been constructed.

2. Five general types of flow curves have been obtained. Type α : true fluids. The viscosity (η) is independent of stress and of the dimensions of the capillary. Type β : η is not independent of stress, but is independent of the dimensions of the capillary. In the majority of cases η falls with rising stress (structural viscosity), but in a few rare cases η rises with stress. Type γ : η is independent of stress, but is not independent of the dimensions of the capillary. In most cases a narrower or longer capillary shows a lower η (due to a breakdown in structure), but in a

few cases the reverse occurs (type ϵ). Type δ : η is not independent of either stress or the dimensions of the capillary.

In the case of systems which are not truly fluid, viscosities are defined under arbitrarily chosen conditions of stress and shear.

3. A microscopic examination of creams has been made for comparison with their rheological properties. Even an amount of breakdown induced by shearing which was too small to be observable microscopically could be demonstrated from the flow curves. Only in the case of comparatively drastic breakdown was there any visible change in the size of the clumps of fat globules.

4. Preliminary comparisons of the flow curves of natural, homogenized, and reconstituted creams do not make it possible to distinguish the different types of cream, although certain general trends have been observed. It is hoped that further work may make possible some such more exact classification.

REFERENCES

- (1) AMBROSE AND LOOMIS: *Physics* **4**, 265 (1934).
- (2) BATEMAN AND SHARP: *J. Dairy Sci.* **11**, 380 (1928).
- (3) BATEMAN AND SHARP: *J. Agr. Research* **36**, 647 (1938).
- (4) FREUNDLICH AND RÖDER: *Trans. Faraday Soc.* **34**, 308 (1938).
- (5) HARTLEY: *Nature* **142**, 161 (1938).
- (6) HATSCHKE AND JANE: *Kolloid-Z.* **39**, 300 (1926).
- (6a) HENING AND DAHLBERG: *New York Agr. Expt. Sta. Tech. Bull.* No. 197 (1932).
- (7) KÖSTER: *Chem. Fabrik* **9**, 381 (1936).
- (8) KURTZ: *J. Phys. Chem.* **33**, 1489 (1929).
- (9) LEIGHTON AND KURTZ: *J. Phys. Chem.* **33**, 1485 (1929).
- (10) LEIGHTON AND LEVITON: *J. Phys. Chem.* **36**, 523 (1932).
- (11) LEIGHTON AND WILLIAMS: *J. Phys. Chem.* **31**, 596, 1663 (1927); **33**, 1480 (1929).
- (12) LEVITON AND LEIGHTON: *J. Phys. Chem.* **40**, 71 (1936).
- (13) MOHR AND OLDENBURG: *Milchw. Forsch.* **8**, 429, 576 (1928).
- (14) PHILIPPOFF: *Kolloid-Z.* **83**, 163 (1938).
- (15) SCHOFIELD AND SCOTT BLAIR: *J. Phys. Chem.* **34**, 248, 1505 (1930); **35**, 1212 (1931); **39**, 973 (1935).
- (16) SCHOFIELD AND SCOTT BLAIR: *Proc. Roy. Soc. (London)* **A138**, 707 (1932); **A139**, 557 (1933); **A141**, 72 (1933); **A160**, 87 (1937).
- (17) SCOTT BLAIR: *J. Rheol.* **1**, 127 (1930).
- (18) SCOTT BLAIR: *An Introduction to Industrial Rheology*. Churchill, London (1938).
- (19) SCOTT BLAIR AND CROWTHER: *J. Phys. Chem.* **33**, 321 (1929).
- (20) WOLL: *Wisconsin Expt. Sta. Ann. Rept.* **12**, 164 (1895).
 BABCOCK AND RUSSELL: *Wisconsin Agr. Expt. Sta. Ann. Rept.* **13**, 73, 81 (1896).
 BOGDAN: *Ann. chim. anal.* **10**, 90 (1905).
 KOBLER: *Arch. ges. Physiol. (Pfügers)* **125**, 1 (1908).
 DUMARESQU: *Proc. Roy. Soc. Victoria* **25**, 307 (1913).
 EVENSON AND FERRIS: *J. Dairy Sci.* **7**, 174 (1924).
 DAHLBERG AND HENING: *New York Agr. Expt. Sta. Tech. Bull.* No. 113 (1925).

SHERWOOD AND SMALLFIELD: J. Dairy Sci. 9, 68 (1926).

ST. JOHN: Ind. Eng. Chem. 19, 1348 (1927).

WHITAKER, SHERMAN, AND SHARP: J. Dairy Sci. 10, 361 (1927).

RAHN AND SHARP: Physik der Milchwirtschaft. Parey, Berlin (1928). This contains a general summary of work prior to 1928.

PYNE AND LYONS: J. Dept. Agr. (Ireland) 27, 121 (1928).

BABCOCK: U. S. Dept. Agr. Tech. Bull. No. 249 (1931).

HENDERSON: Proc. Intern. Assoc. Milk Dealers, 29th Annual Convention, Lab. Section, p. 21 (1936).

RIPA-U-TILICI AND DRĂGULESCU: Z. Untersuch. Lebensm. 72, 121 (1936).

GUTHRIE: Cornell Univ. Agr. Expt. Sta. Bull. No. 666 (1937).

OPTICAL ANISOTROPY AND THE STRUCTURE OF CELLULOSIC SHEET MATERIALS¹

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In this communication the approach to the optical anisotropy of xerogel sheets described by McNally and Sheppard (4) is extended to give a more complete representation of their birefringence. This property is now expressed in quantitative rather than in graphical form, the directions of the indices are defined, and, whenever profitable, the structural interpretation is supplemented with x-ray diffraction evidence.

METHOD

The birefringence is evaluated by observation of the birefringence at known angles of refraction as the refracted beam is swept, by rotation of the specimen, through as large an angle as possible in two of the three principal sections of the biaxial sheet. This, with suitable graphical extrapolation, allows the appraisal of the differences between the refractive indices. The uniaxial sheet for which only one rotation is required is considered the special case. At any given angle of refraction in the principal section,

$$\delta = \frac{d}{\cos r} (n_1 - n_2) \quad (1)$$

where δ is the observed birefringence, d , the thickness of the sheet, n_1 and n_2 , the refracted indices of the ray at the angle r , and r , the angle of refraction, is defined by the relation

$$\mu_1 \sin \theta = \mu_2 \sin r \quad (2)$$

where μ_1 and μ_2 are the indices of refraction of the medium and specimen, respectively. The curves obtained by plotting $\delta \cos r/d$ against r^0 are shown in figure 1: the curve which crosses the zero birefringence axis identifies the section containing the optic axes; the other is readily recognized. Even with the extended curves now available, accurate extrapolation is not possible in their present form, but this is easily accomplished when $\delta \cos r/d$ is expressed as a straight-line function of the angle of re-

¹ Communication No. 700 from the Kodak Research Laboratories.

fraction. This has been done from the following considerations: In each wave surface section, the birefringence is in every case the difference between a constant and varying index, i.e., $n_1 - n_2$. The general relation between the angle of refraction and the birefringence in each section must have the form

$$f(r) = f(n_1) - n_2 \quad (3)$$

In the section the constant index n_2 is reciprocally associated with the circle radius. The variation of the other index, n_1 , is again dependent

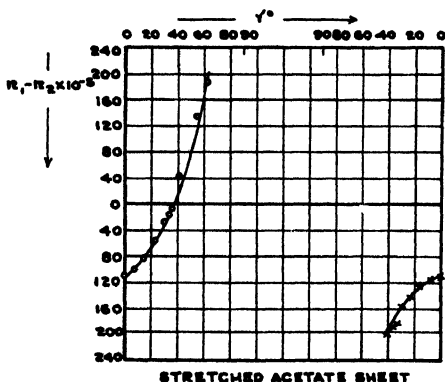


FIG. 1

FIG. 1. Birefringence curve with angle of refraction

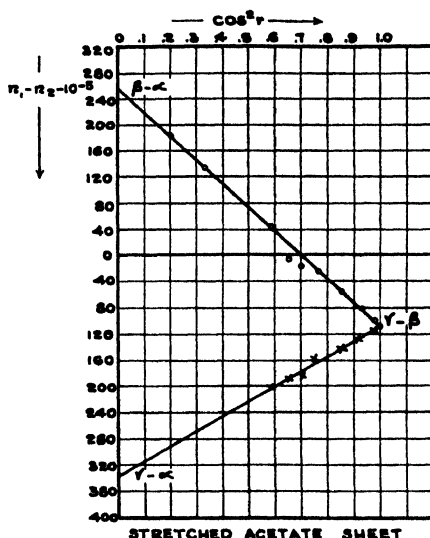


FIG. 2

FIG. 2. Birefringence curve with \cos^2 of angle of refraction

reciprocally on the normal to the tangent to the wave front at the point of emergence of the ray. Thus,



where ON is normal to the tangent to OR , the ray direction at R . The variation of $\frac{1}{ON}$ with the angle of refraction may be computed, when a and b , the semiaxes of the elliptic section whose reciprocals correspond to

the maximum and minimum refractive indices, do not differ to a great extent, as is the case with sheet materials

$$n_1 - n_2 = \frac{1}{b} - \frac{\mu}{b} \cos^2 r - n_2 \quad (4)$$

where $1 + \mu = K$ and $K = a/b$. Thus, $n_1 - n_2$ is a linear function of $\cos^2 r$.

Obviously, if r is 90° , equation 4 becomes $\frac{1}{b} - n_2$.

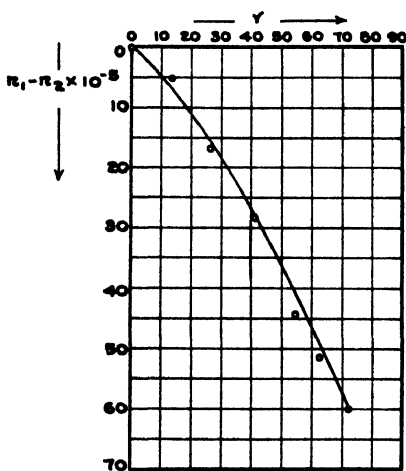


PLATE-COATED
CELLULOSE TRIACETATE

FIG. 3

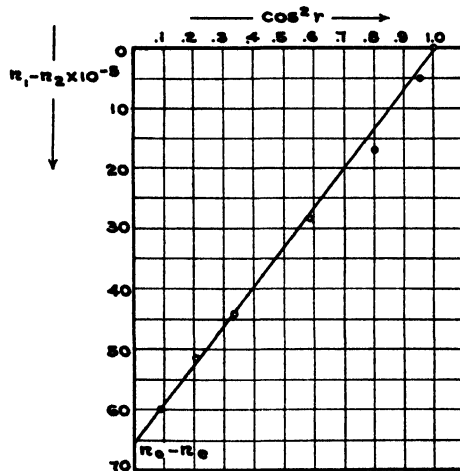


PLATE-COATED
CELLULOSE TRIACETATE

FIG. 4

FIG. 3. Birefringence curve with angle of refraction

FIG. 4. Birefringence curve with \cos^2 of angle of refraction

It can be shown also that the expression is valid, within the limits of the approximation, if r is 0° . Then equation 4 becomes

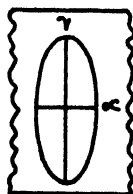
$$\frac{1}{b} (1 - \mu) - n_2$$

and

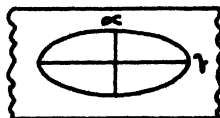
$$\frac{1}{a} = \frac{1}{b} \cdot \frac{1}{1 + \mu} \cong \frac{1}{b} (1 - \mu)$$

For this expression, which makes possible accurate extrapolation of the birefringence curves, thanks are due to Dr. Herzberger of these Laboratories. This transformation of the curves of figure 1 is shown in figure 2, and a similar transformation in the case of a negative uniaxial sheet of cellulose triacetate is shown in figures 3 and 4. In upwards of three hundred cellulosic sheets examined in these Laboratories, this relation of $\delta \cos r/d$ and $\cos^2 r$ has been found sufficiently valid.

It is thus possible to present the results, not, as before (4), in graphical, but in quantitative form. This, together with the location of the index ellipse in the film with reference to stresses applied, etc., provides the requisite data for the fullest structural interpretation. This is demonstrable with two general cases without reference to the position of the optic axes.



I



II

TABLE 1

Values obtained from the two rotations when extrapolated to 90°

(1) CASE	(2) PLANE OF ROTATION	(3) BIREFRINGENCE AT $r = 0^\circ$	(4) BIREFRINGENCE AT $r = 90^\circ$	NO.
I.....	$\gamma\alpha$	$\beta - \alpha$	$\gamma - \beta$	1
I ₁	$\gamma\beta$	$\beta - \alpha$	$\gamma - \alpha$	2
II.....	$\gamma\alpha$	$\gamma - \beta$	$\beta - \alpha$	3
II ₁	$\alpha\beta$	$\gamma - \beta$	$\gamma - \alpha$	4

The plane of the sheet is normal to the paper and the line of observation is normal to the sheet, i. e., normal incidence is along γ in case I and α in case II, corresponding to r , the angle of refraction of 0°. The values obtained from the two rotations when extrapolated to 90° are summarized in table 1.

While one rotation in the axial section $\gamma\alpha$ is sufficient to determine $\gamma - \alpha$, the maximum value of the birefringence, by the addition of columns 3 and 4 for Nos. I and II, the presence of the second rotation I₁ and II₁ allows a second estimate; in practice, an average value is selected.

The determination of the optic sign and the orientation of the indices may be facilitated by a study of the interference patterns and of the addition and subtraction colors with a first-order red plate of several, similarly orientated thicknesses of the sheet. From such a preliminary examination of stretched acetate sheeting, the results given in table 2 are obtained. This, together with the deduced difference in index from the extrapolated curves, enables the complete representation shown in table 3 to be made.

The estimated accuracy of the method is 10 per cent for values of $\gamma - \alpha$

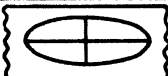
of 60×10^{-6} and greater; for lower values, it ranges from 10 to 20 per cent. The estimation of the optic axial angle may show a 20 per cent variation at angles of less than 15° .

The apparatus used in these experiments consists essentially of a unit provided with three axes of rotation for the sample under examination. Since its distinctive feature allows for immersion of the sample during its rotations about the extinction position, it is possible, therefore, by a suitable choice of immersion media to obtain from equation 2 a reasonable number of values of r . A necessary precaution is the avoidance of any swelling or solvent action by the medium,—an eventuality which may be detected by change of birefringence with time. The apparatus, which is

TABLE 2
Preliminary examination of stretched acetate sheeting

FILM	CONOSCOPIC OBSERVATION					PARALLEL LIGHT
	Interference pattern					Vibration direction of slow ray in film plane, 1st-order red plate
	Type	Sign	Line of observation normal to film	Axial angle	Axial section	
Stretched acetate	Biaxial	—	Acute bisectrix	Small	Direction of stretch	Direction of stretch

TABLE 3
Complete representation of stretched acetate sheeting

FILM	TYPE	SIGN	AXIAL ANGLE 2V	$\gamma - \beta$ $\times 10^{-3}$	$\beta - \alpha$ $\times 10^{-3}$	BIREFRINGENCE $\gamma - \alpha$ $\times 10^{-3}$	ORIENTATION OF INDEX ELLIPSE IN FILM THICKNESS
Stretched acetate	Biaxial	—	66°	110	238	348	

not unique, is outlined in figure 5. Such an arrangement facilitates change and control of the immersion medium. A Polaroid filter is employed as polarizer, and, while a choice of compensators is possible, the type most frequently used in these measurements is the double quartz wedge whose components have their "slow" vibration directions at right angles (4). This instrument when mounted with analyzer allows a rapid measurement. For certain purposes the Berek compensator may be used; it is more sensitive with low birefringence values than the former and may be used to determine "slow ray" vibration directions, etc. Unlike the wedge type, however, which employs a direct scale reading, the latter must be adjusted to compensation for each reading, and with a number of films to be examined the time involved may be a consideration. The source of

light is the type H3 mercury lamp supplied by the General Electric Company; with the requisite filters, a good range and intensity of lines are given. Such a source is preferable to a monochromatic one which does not allow rapid recognition of the influence of dispersion on the birefringence, an influence which is frequently appreciable in plasticized sheets. The filters employable are listed in table 4.

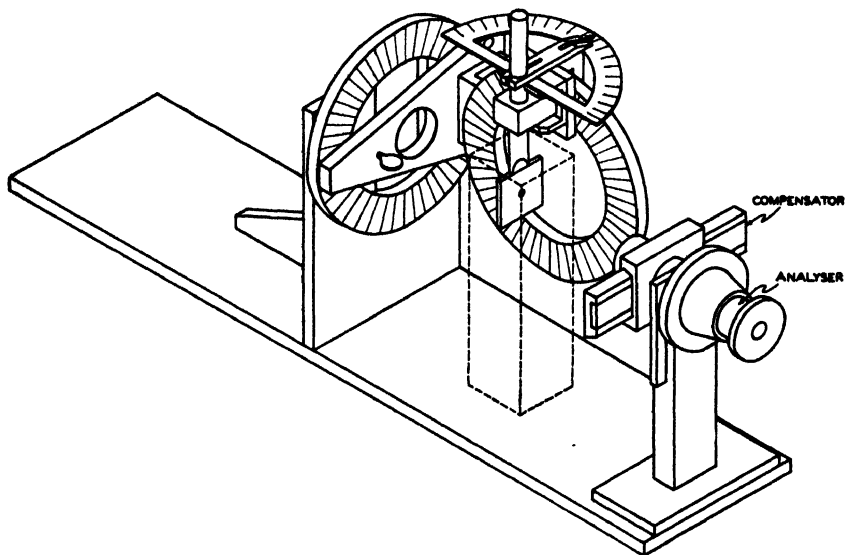


FIG. 5. The apparatus

TABLE 4

Description of filters

LINE	FILTER
λ .	
4360	Corning No. 71
4916	2× Wratten 75
5416	Wratten 77A + No. 58
5790	Wratten 22 Monochromat
6900	Wratten 70 + No. 16

Most of the measurements are made with λ 5790 Å. A desirable precaution in such an assembly is the placing of gelatin filters behind the Polaroid filter; the gelatin sheet itself is birefringent-uniaxial with the optic axis normal to the sheet, and if placed in front of the polarizer may introduce an appreciable error if accidentally tilted from the vibration plane of the system. To facilitate computation graphs of the ratio μ_1/μ_2 against $\cos r$ and $\cos^2 r$ for selected values of θ , the angle of incidence may be constructed from equation 2.

For immersion media, α -chloro- and α -bromonaphthalenes have been employed, but with side chains longer than butyrate the usual salt solutions must be used. Refractive indices were measured with the Abbe refractometer. As is customary in polariscopic observations of this kind, the directions of vibration of the compensator and specimen are placed in the diagonal or 45° position to those of the crossed polarizer and analyzer.

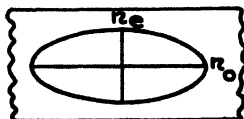
RESULTS

The two main influences on the birefringence of cellulose ester sheets are (1) the nature of the side chain attached to the principal valence chain, and (2) the micellar or crystallite orientation. These two effects cannot always be separated, because the side chains may influence not only the anisotropy of the molecule but also the orientation of the micellar units. An instance where the former clearly predominates is shown by the change in birefringence with the diminishing acetyl content of cellulose acetate. The results with plate-coated uniaxial negative sheets whose average

TABLE 5
Change in birefringence with diminishing acetyl content of cellulose acetate

ACETYL CONTENT	BIREFRINGENCE $n_e - n_o \times 10^{-3}$
44.6	-66
40.6	-246
39.3	-580
35.0	-620
27.0	-700

thickness was 0.13 mm. are shown in table 5. The index ellipse for these sheets is placed in the thickness of the film:



Thus, the increase in negative birefringence shown in table 5 is due to an increase in n_o , whose vibration direction is the plane of the sheet. An effect of this magnitude must be chiefly the result of molecular changes and not of any changes in micellar orientation.

With completely esterified products it is assumed that the anisotropy of the orientated crystallites or micelles may be interpreted in terms of a similar orientation of molecules. This is permissible only if the aliphatic side chains of the crystallite are perpendicular to the glucopyranose residues not only on the same but also on neighboring parallel molecules. There

is good experimental support for acceptance of this assumption from the x-ray diffraction studies of J. J. Trillat (7) on a homologous series of cellulose esters.

In general, while a weakly anisotropic molecule can never give a strongly birefringent crystal, a strongly anisotropic molecule may give either a strongly or weakly birefringent crystal, according to the crystalline molecular arrangement. There may be cases, therefore, when x-ray diffraction evidence is absent, in which the aforementioned assumption cannot be made. X-ray evidence is fairly conclusive in the identification of film crystallites as similar to, or derived from, their fibrous counterparts (5). Birefringence of the sheet, however, results from the orientation of such units in the aggregate, and in its interpretation consideration is given to the resultant molecular orientation. With such cellulosic sheets the index ellipse is placed normal to the plane of the sheet without serious error, and the birefringence interpreted in terms of the molecular architecture which the micellar orientation determines.

TYPES OF ORIENTATION IN XEROGELS

There are three classes of micellar or crystallite orientation which are idealized for descriptive purposes: *viz.*, (a) uniplanar orientation, (b) selective uniplanar orientation, and (c) directional orientation. The first two terms are taken from Sisson's description (6), but it is felt that his description of class *c* as uniaxial orientation is, in this application, an unfortunate choice since, in many instances, the result is optically biaxial.

Uniplanar orientation involves a completely random orientation except for the restriction that the principal valence chains lie in one plane,—in general, the plane of the film. The result is optically uniaxial. Selective uniplanar orientation places the added restriction on uniplanar that the side chains are not at random but are in a fixed direction. This result is again uniaxial. Directional orientation restricts the direction of the principal valence chains to one direction; the result is usually optically biaxial, but complete directional orientation in one direction should in the absence of the other type give a uniaxial film with the optic axis in this direction.

Uniplanar orientation

While the three types of orientation cannot always be separated, the increasing birefringence with diminishing sheet thickness is clearly the result of increased uniplanar orientation. This effect is particularly evident with slightly hydrolyzed esters, as is shown by such an acetate propionate (see table 6).

Selective uniplanar orientation

This type of orientation is more evident with fully esterified sheets than in those containing a proportion of hydroxyl groups. The side-chain

spacings, identifiable from Trillat's results, show marked fibering with the x-ray beam in the plane of the sheet. As a consequence of this arrangement, the directional influence of the side chains on the refractive index must be considered, as shown in table 7. The introduction of side chains longer than acetate, as in acetates butyrate and propionate, increases the index normal to the sheet to the extent of a reversal of sign. Cellulose caprylate, on the other hand, possesses a relatively high negative birefringence,—a result that suggests a proportion of side chains in the plane of the sheet.

TABLE 6
Increasing birefringence with diminishing sheet thickness

THICKNESS	BIREFRINGENCE $n_s - n_o \times 10^{-4}$
mm.	
0.010	203
0.028	190
0.051	150
0.076	140
0.127	132

TABLE 7
Directional influence of the side chains on the birefringence

ACETATE	BIREFRINGENCE $n_s - n_o \times 10^{-3}$
Acetate	-66
Acetate propionate	+46
Acetate butyrate	+25
Butyrate	-14
Caproate	-62
Heptoate	-76
Caprylate	-100

Directional orientation

This type results from unidirectional stresses. If complete, the long chains would be aligned in the direction of stress in a similar manner to those of the fiber. Its interpretation in terms of micellar orientation from birefringence measurements necessitates the elimination of any contribution to the double refraction from deformation of valence bonds, and, in the present observations, this was accomplished by the application of tensions to the incompletely cured sheet. In this state an appreciable amount of solvent is retained, the sheet possessing the elastic properties of a swollen gel. Table 8 shows the difference in index in and normal to the plane of the sheet of plate-coated material and those stretched while still retaining solvent. Since the sheets on extension become biaxial, an

effective comparison can only be made by noting the difference between the greater index n'_γ in and that normal n'_α to the plane of the sheet. When the latter has the greater index, the birefringence is preceded with a negative sign. In column 3 the difference in indices, $n'_\gamma - n'_\beta$, in the plane of the sheet is given. The nomenclature n'_α , n'_β , and n'_γ is used only for comparative purposes, and is not always identifiable with the customary n_α , n_β , and n_γ . Comparison of columns 1 and 2 shows that materials that give negative plate-coated sheets show a reduction of this birefringence in the stretched sample. With positive sheets there is a slight increase or little change. In evaluating this comparison it is necessary to consider the influence of extension on this index in the plane of the sheet. It appears reasonable to assume that the "greater index" n'_γ in the plane of the sheet is larger than the ordinary index in the plate-coated sheets. Any alignment of the principal valence chains or a greater orientation of

TABLE 8
Differences in birefringence between plate-coated and stretched sheets

CELLULOSE ESTER	(1) PLATE COATING $n_\beta - n_\alpha \times 10^3$	(2) STRETCHED SHEETS		(3)
		$n'_\alpha - n'_\gamma \times 10^{-3}$	$n'_\gamma - n'_\beta \times 10^{-3}$	
Triacetate	-66	-21		5
Acetate propionate	46	50		11
Acetate butyrate	25	25		4
Butyrate	14	16		13
Heptoate	-76	-50		130
Caprylate	-400	-200		2

glucopyranose rings in the plane of the sheet would tend to increase the index in this plane. X-ray diffraction evidence, in general, supports this view; the contrast in ring fibering between plate-coated and stretched sheets of cellulose butyrate is shown in figure 6. Triacetates show little difference, but the increased ring fibering is clearly shown in the diagrams of acetate propionate and acetate butyrate. Comparison diagrams of sheets stretched to the same extent, 15 to 20 per cent, when the solvent has been removed as far as possible, show much less fibering than the two aforementioned types. On this view the birefringence results are readily explained, for, if extension results in an increase in the index n'_γ in the plane of the sheet, a reduction in negative and little change or an increase in positive birefringence can only be explained by an increase in n'_α , which, in turn, is attributable to increased selective uniplanar orientation. It is concluded that a second influence of stresses on such open structure sheets is the forcing of side chains perpendicular to the direction of stress.

A similar comparison of the "slow ray" vibration direction in the film produces a provocative result. With plate-coated sheets such a slight orientation may not always be evident, even when the Berek compensator or first-order red plate is used, and, as far as the quantitative expression is concerned, they are all considered uniaxial. The coating direction in

X-Ray Beam in Plane of Sheet

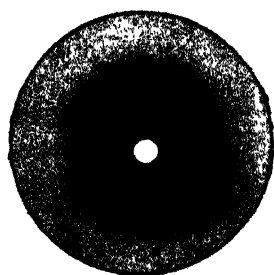
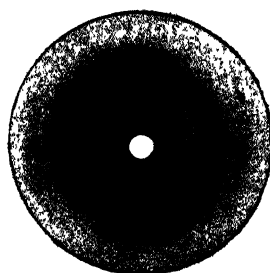


Plate-Coated



Stretched

FIG. 6. Cellulose butyrate sheeting showing "fibering" of side-chain spacing

TABLE 9
Slow ray direction

CELLULOSE ESTER	PLATE-COATED REFERRED TO COAT- ING DIRECTION	STRETCHED REFERRED TO STRESS DIRECTION
Triacetate	⊥	⊥ to =
Acetate propionate	⊥	⊥
Acetate butyrate	⊥	⊥
Butyrate		⊥
Heptoate		⊥
Caprylate	---	⊥

such coatings is perpendicular to the spreading knife edge (table 9). All stretched sheets give a slow vibration normal to the direction of stress. This may be explained from the similar orientations observed in the plate-coated sheets in observable cases, suggesting that an initial effect of stress may be the alignment of chains normal to its direction, an effect which is predetermined by the tendency of these chains to lie parallel to the

coating knife edge; it is only at considerable elongations that the triacetate shows a slow vibration in the direction of stretch.

DISCUSSION AND CONCLUSIONS

The appreciable increase in negative birefringence occasioned by the introduction of hydroxyl groups is in marked contrast to the results obtained by Kanamaru (3) on a series of progressively acetylated fibers. His observations, made by means of the immersion method, show negligible change over a wide range of acetyl contents—15 to 45 per cent—and are attributed to the topochemical nature of the acetylation process, giving a completely acetylated micellar surface, which, by this experimental method, determines the birefringence. It should be noted that these acetylated ramie fibers, obtained by a progressive increase in the time of reaction, show, in comparison with acetate sheets, three relevant differences: Firstly, the sheets are obtained by partial hydrolysis of the fully esterified product, which results in not only a greater proportion of primary alcoholic groups but also the presence of hydroxyl groups on the micellar surface. Secondly, these sheets are obtained by at least partial dissolution and subsequent regeneration of the crystallites with a measure of intracrystallite change (5). Thirdly, and significantly, the presence in sheets of planar orientation, implying the presence of a side-chain orientation in comparison with a more random orientation in fibers, makes quantitative comparison impossible. Bernal and Crowfoot (1) suggest that, in testosterone and androsterone, the presence of hydroxyl groups perpendicular to the planar system may be responsible for the increased index in that direction. On this view it is possible to speculate that the relatively high negative birefringence promoted by partial hydrolysis of the ester groups indicates the presence of a proportion of hydroxyl groups in the plane of the sheet. The evidence available suggests, but does not definitely prove, that the presence of a small proportion of hydroxyl groups diminishes the selective uniplanar orientation. X-ray diffraction diagrams show that, in comparison with the introduction of a similar proportion of propionyl or butyryl groups, the hydroxyl group produces much more intracrystallite lattice disorganization. Ring fiber structure is much less in evidence, but this does not exclude its presence. One may suggest that the relatively great disorganizing effect on the structural manifestations occasioned by such an introduction of a proportion of hydroxyl groups may be associated with hydrogen bridge formation by hydroxyl groups in proximity. The significance of this type of bonding in cellulose and other long-chain molecules has been pointed out by Huggins (2), and it is easy to visualize inter- and intracrystallite bridging promoting the less organized arrangement. On this view the effect of partial hydrolysis of a cellulose ester gives rise to two stereochemically opposing tendencies: namely, the align-

ment of the aliphatic side chains and the relatively powerful bridging of the hydroxyl groups.

The influence of thickness on the birefringence of sheets indicates also that, with increasing thickness, the planar orientation decreases. Thus, thicker sheets are biaxial where the orientating influence of the spreading knife edge becomes more effective and the rate of coating becomes increasingly influential on the birefringence (5). If, in the greater thicknesses, symmetrical distribution of "dope" were possible, an isotropic material would result. It is this dimensional influence on the planar orientation that invalidates comparisons with the optical anisotropic properties of the bulkier samples employed for photoelastic measurements.

The introduction of side chains longer than acetyl increases the index normal to the sheet, and with increasing length, as in caproate and heptoate, a tendency to an increase in the index in the sheet occurs. The first effect is paralleled by the observations of Bernal and Crowfoot (1) on the influence on the birefringence of side chains attached to a saturated ring system of a series of sex hormones. They suggested that the introduction of methyl groups perpendicular to the plane of a ring system produced weak positive birefringence. There is no definite x-ray diffraction indication of differences in a selective uniplanar orientation between triacetate, acetate propionate, and acetate butyrate, and the differences in optical anisotropy may be attributed to the difference in side chains attached to each molecule. The high negative birefringence of cellulose caprylate and the reduction thereof on extension finds some explanation from the results of Trillat's investigations on the structures of a series of aliphatic esters of cellulose. From these studies Trillat identified the side-chain spacing, firstly, by its increasing distention with increasing length of aliphatic chain and, secondly, by noting similar spacing increases of the series of free aliphatic acids and their lead salts. He also demonstrated that the "crystallinity" diminished rapidly beyond propionate; this he attributed to the diminishing cohesive forces between the principal valence chains, owing to their being pushed apart by the aliphatic side chains. Furthermore, when cellulose caprylate film is stretched to 100 per cent of its original length, a marked discontinuity in the side-chain spacing is noted when the plane of the film is perpendicular to that of the diagram. This suggests that the reduction of the negative birefringence on extension is due to the forcing of the side chains perpendicular to the plane of the film. On the other hand, the high negative value of the plate-coated material at least indicates that the aliphatic side chains are in the plane of the sheet. Any other orientation, such as normal to the plane of the sheet, would tend to develop, first, diminishing negative and then possibly positive birefringence. It may be suggested that this tendency,

involving a tilting of the glucopyranose rings of the long chains, may also explain the birefringence values of the caproate and heptoate.

The influence of unidirectional stresses on the sheet structure produces a more marked selective uniplanar orientation when the sheet is in the swollen condition. A somewhat similar observation has been made by Sisson (6), who noted the development of "selective uniaxial orientation" as stretched synthetic cellulose membranes approached the film structure. Similar x-ray diffraction evidence has been given by Trillat (8) on cellulose acetate. Presumably, the application of tensions to the open structure of the solvent-retaining sheet produces the more organized structure because of the greater freedom to orientate.

The result that the "slow ray" vibration direction in the plane of the film of the fully esterified stretched sheets is normal to the direction of extension may be attributed to at least three factors: (1) The remaining side chains in the plane of the sheet may be sufficient to contribute to the greater polarizability in this direction. Some support for this view may be gathered from the result that cellulose triacetate fibers are negative; the vibration of the ordinary index in the plane of the side chains is that of the slow ray. (2) The long chains may be, in part, aligned normal to the direction of stretch,—a condition that may well be predetermined by the orientating influence of the spreading knife edge. (3) There may be marked discontinuities in the orientation throughout the thickness of the film; it is probable that a highly organized structure exists near the sheet surfaces approaching a more random structure in the center. The nature of the orientated region may determine the slow ray direction.

It may be noted that isolated direct quantitative comparisons of the birefringence of chemically different sheets for the purposes of structural interpretation are spurious. Thus, despite the greater birefringence of the partially hydrolyzed esters, there is reason to believe that the fully esterified, though less birefringent, materials possess the higher degree of crystallite organization. Diminishing birefringence of negative sheets may be the result of increased disorganization in the plane of the sheet or of increasing index normal to this plane, due to increasing organization. X-ray diffraction and subsidiary optical evidence generally permit a decision on this alternative.

It is also clear from these results that, with an appropriate introduction of side chains, the sheet may appear optically isotropic if selective uniplanar orientation is present. Such a sheet would be well organized despite the absence of birefringence arising from the balanced polarizabilities in and normal to the plane of the sheet. Cellulose butyrate illustrates the possibilities in this direction. In general, however, these sheets should be regarded as anisotropic because of their intrinsic property of planar orientation. It is possible to produce a quasi-isotropy by

introduction of a second component, e. g., camphor in cellulose nitrate, but differences in optical dispersion preclude the absence of birefringence over a range of visible wavelengths.

The chief advantage of such birefringence measurements is a practical one. They may be made whether the sheet gives instructive x-ray diffraction diagrams or not, and the latter alternative is a frequent occurrence with cellulose ester sheets. Sisson's (6) studies on synthetic cellulose membranes exemplify the x-ray method at its best; the diagrams are well resolved with the different types of orientation clearly shown, and for a structural interpretation birefringence measurements, apart from a theoretical interest, would be superfluous.

It is hoped to deal with the influence of solvents and plasticizers in a later publication. These influences, while real, do not alter the general conclusions of this paper.

SUMMARY

The evaluation of the birefringence of sheet materials is described and the general considerations in its structural interpretation are discussed and demonstrated.

The writer desires to express his sincere thanks to Dr. S. E. Sheppard for his experienced and encouraging counsel during these investigations, to Mr. S. S. Sweet for valuable assistance in the coating of diverse sheet materials, and to Dr. P. T. Newsome for helpful discussion of the subject matter.

REFERENCES

- (1) BERNAL, J. D., AND CROWFOOT, D.: *Z. Krist.* **93**, 464 (1936).
- (2) HUGGINS, M. L.: *J. Org. Chem.* **1**, 407 (1936).
- (3) KANAMARU, KISOU: *Helv. Chim. Acta* **17**, 1429 (1934).
- (4) McNALLY, J. G., AND SHEPPARD, S. E.: *J. Phys. Chem.* **34**, 165 (1930).
- (5) SHEPPARD, S. E., AND NEWSOME, P. T.: *J. Soc. Chem. Ind.* **56**, 256T (1937).
- (6) SISSON, WAYNE A.: *J. Phys. Chem.* **40**, 343 (1936).
- (7) TRILLAT, J. J.: *J. phys. radium* [7] **5**, 207 (1934).
- (8) TRILLAT, J. J.: *J. phys. radium* [6] **10**, 370 (1939).

THE DEVITRIFICATION TEMPERATURES OF SOLUTIONS OF A CARBOHYDRATE SERIES

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Several liquids, when cooled at a velocity of the order of some hundred degrees per second, become vitreous. The glasses so obtained devitrify, that is, crystallize, when upon warming they reach certain temperatures called the devitrification temperatures. The latter are, therefore, the temperatures at which a body passes from the vitreous to the crystalline state (2). Unlike the melting or the boiling temperatures, they are not sharply defined points but extend over a range, devitrification being slow at the lower end of the range and gradually faster at the upper end. The devitrification temperatures should therefore be expressed in the form of temperature-time relations.

By use of the method of immersion of thin layers in liquid air for rapid cooling, the vitreous state was obtained in various aqueous solutions: gelatin, albumin, gums, sugars, inorganic salts, etc. (1). The investigation of the devitrification temperatures of such solutions was then begun, and it was observed that there is apparently a relation between these temperatures and the structural complexity of the solute. The present report is concerned with that relation as shown in sugar solutions.

Vitreous sugar solutions are transparent; when they devitrify they become intensely opaque. In polarized light, between crossed Nicols, the vitreous substance is dark; after devitrification it reestablishes light. To determine the temperature-time curve, the change in the opacity of the material in ordinary light was used as a criterion of devitrification.

A small drop of the sugar solution to be studied was enclosed between two glass plates 0.1 mm. thick, maintained at a distance of 0.1 mm. from each other by two glass strips of that thickness interposed between the plates. This preparation, held in a clip, was first immersed in liquid air for vitrification; it was then withdrawn and, after 8 sec. had been allowed for the evaporation of the liquid air carried along, it was immersed in a constant-temperature bath of isopentane contained in a transparent (un-silvered) Dewar flask. Isopentane was used on account of its immiscibility with water. The increase in opacity was observed against a 100-watt lamp placed beyond two pieces of ground glass at a distance of 25

cm. from the preparation. Five arbitrary degrees of opacity were distinguished by comparing the devitrifying material with an opacity scale made by depositing layers of various thicknesses of white paint on a piece of glass. For establishing the fifth degree—the only one which is concerned in this paper—the opacity of a preparation frozen at a few degrees below zero was taken. The temperature was measured by an alcohol thermometer graduated to -50°C . in fifths of degrees and recalibrated at 0°C . against an Anschütz thermometer (with P.T.R. certificate). The readings were corrected for incomplete immersion of the stem after the correction values had been established by comparison of the incompletely immersed thermometer with another of the same make, completely immersed and itself recalibrated at 0°C . The duration of devitrification was measured with a stop watch.

The results obtained with glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, at 2 *M* concentration, with sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, at 2 *M* concentration, with raffinose, $\text{C}_{18}\text{H}_{32}\text{O}_{16} \cdot 5\text{H}_2\text{O}$ at 1 *M* concentration, and with dextrin, $(\text{C}_6\text{H}_{10}\text{O}_5)_x$, at $2M/x$ concentration are graphed in figure 1. The products used were of the purest grade prepared by the Pfanstiehl Chemical Co.

These sugars were chosen on account of the number of their carbon atoms, which is six or a multiple of six, but they are not entirely comparable otherwise: raffinose crystallizes with five molecules of water, the others are anhydrous; glucose has a free aldehydic group, the polysaccharides have none; the number of hydroxyl groups does not vary proportionally to the number of carbon atoms; glucose seems to possess only a six-membered ring, while sucrose probably has a five-membered ring and a six-membered ring; etc.

In each of the carbohydrate solutions that were studied—and the same is true of many other solutions—the physical properties related to crystallization changed from one range of concentrations to another, there being three well-observed ranges: (1) A high concentration range in which the solution did not freeze at any temperature, for example, 3 *M* sucrose; devitrification was then impossible. (2) A low concentration, 2 *M* for sucrose, at which the solution could be vitrified and devitrified. On devitrification, the preparation took on an amber color when observed in transmitted light. The opacity described above consists, then, in a deepening and darkening of the originally transparent, then translucent, amber layer. This appearance of the preparation and the gradual increase in opacity, which can well be observed in these conditions, are, no doubt, due to the fine grain of the crystals. (3) An intermediate concentration, 2.4 *M* for sucrose, in which the pattern of the devitrifying material is different from that just described; the amber color is absent, the increase in opacity does not take place with the smooth gradation of the less concentrated solution, and the crystalline structure seems to consist of a coarser grain. The temperatures at which this type of devitrification

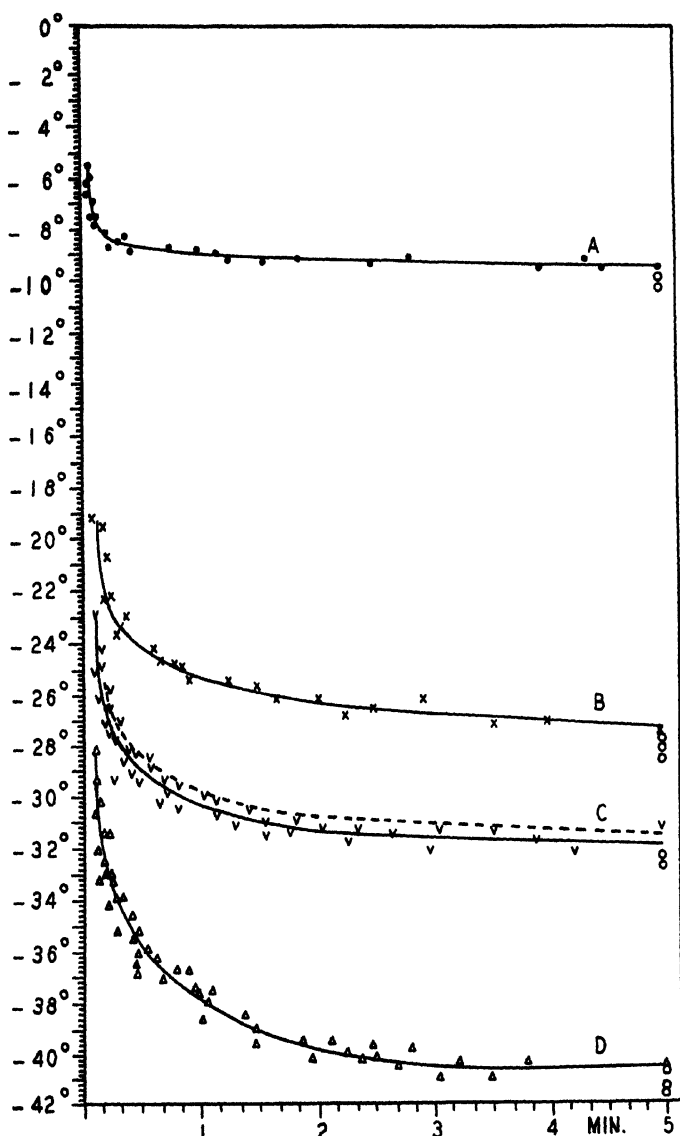


FIG. 1. Plot of time against devitrification temperature. Curve A, 2M/x dextrin; curve B, 1M raffinose; curve C (unbroken line), 2M sucrose; curve C (dashed line), 1M sucrose; curve D, 2M glucose. The circles at the right-hand end of each curve indicate that the solution was not devitrified in 5 min.

occurs are lower than those of the former type; for sucrose they are more than 15°C. lower.

In the present work only the devitrification temperatures of solutions of the lower concentration range are compared. An attempt was made to use for that purpose the same molecular concentration for all the sugars, but this was impossible. While a concentration of 2 *M* was convenient for glucose and sucrose, it could not be used for raffinose which, at that concentration, is in the upper range and does not freeze at any temperature. On the other hand, a concentration of 1 *M* was convenient for

TABLE 1

Time for devitrification of sucrose solutions at various temperatures

TEMPERATURE	TIME FOR DEVITRIFICATION OF 1 <i>M</i> SUCROSE	TIME FOR DEVITRIFICATION OF 2 <i>M</i> SUCROSE
°C.	seconds	seconds
-26.4	11	8
-26.8	15	13
-27.6	23	20
-27.9	23	17
-28.3	30	25
-29.0	38	32
-29.4	49	42
-30.0	63	48
-30.4	83	71
-30.8	120	88
-31.1	175	95
-31.5	250	185
-31.7	400	235

TABLE 2

Devitrification temperatures in a standard time of five minutes

SUGAR SOLUTION	CONCENTRATION	TEMPERATURE	NUMBER OF CARBON ATOMS
		°C.	
Glucose.....	2 <i>M</i>	-40.6	6
Sucrose.....	2 <i>M</i>	-31.8	12
(Sucrose.....	1 <i>M</i>	-31.4	12)
Raffinose.....	1 <i>M</i>	-27.2	18
Dextrin.....	2 <i>M</i> / <i>x</i>	-9.4	6 <i>x</i>

raffinose and sucrose, but glucose could not be vitrified at that concentration, since it froze on being immersed in liquid air. So the following were selected for study: 2 *M* glucose, 2 *M* sucrose, 1 *M* raffinose, and 2 *M*/*x* dextrin. To render the comparison between raffinose and sucrose possible, a determination of the devitrification temperatures of 1 *M* sucrose was also made (the dashed line on the graph).

There is a very slight difference in devitrification temperatures for a

considerable change in concentration within a given concentration range. By mounting two drops, one of 1.4 *M* and the other of 1.6 *M* sucrose, on the same preparation and observing simultaneously the change in opacity, no difference could be observed between them. The same procedure, however, allowed one to detect a difference of about 0.4°C. in the devitrification temperatures of 1 *M* and 2 *M* sucrose. The figures obtained for the devitrification times of 1 *M* and 2 *M* sucrose at various temperatures are given in table 1. The difference in opacity between the two concentrations was mostly noticeable during the first stages of the darkening of the amber-colored preparation; it became less at the last stages. The higher concentrations caused a depression of the devitrification temperatures, a fact which perhaps is to be attributed to the same cause as the depression of the freezing point.

Taking 5 min. as a standard devitrification time, the devitrification temperatures of the sugar solutions studied range as shown in table 2.

According to preliminary results, solutions of substances of high molecular weight, like the gums, agar agar, and gelatin, have a devitrification temperature in the neighborhood of $-10^{\circ}\text{C}.$, while solutions of substances of low molecular weight, such as formaldehyde, ethylene glycol, and glycerol, devitrify between -80° and $-60^{\circ}\text{C}.$ The various radicals exert a definitely different influence on the devitrification temperatures, and this influence must be studied before any attempt at establishing a quantitative relation of more general nature can be made.

REFERENCES

- (1) LUYET, B. J.: Bull. Am. Physical Soc. **12**, No. 7, 7 (1937); **14**, No. 2, 29 (1939).
- (2) TAMMANN, G.: The States of Aggregation, p. 275. Translated by R. F. Mehl. D. Van Nostrand Co., New York (1925).

LATERAL COHESION IN PROTEIN MONOLAYERS¹

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The formed structures of animal cells and tissues are composed primarily of protein and are presumably laid down by alteration of soluble protein. Each type of structure,—for example, membranes or fibrils,—may have its specific mode of formation and series of precursor compounds, as in fibrin clotting, yet the physical processes involved may be of very general occurrence throughout biological systems. Such a process is seen in the adsorption of protein molecules at an interface, with subsequent rearrangement of structure and the formation of bonds linking the units, which are themselves polymers of amino acids, in another degree of polymerization. To obtain information concerning the processes by which interfacial structures can be produced from solutions containing protein one may study the properties of protein monolayers. Such films offer the possibility of a great degree of control over the relation of molecules to each other and to the aqueous subsolution. Since the cohesion of molecules within the plane of the film is of particular interest from the point of view of membrane formation, a quantitative method was devised for studying the viscosity and elasticity of unimolecular films as an index of the lateral bonding of molecules.

This paper presents results obtained by applying this method to unimolecular films of casein and of nerve axis cylinder protein. Findings with cholesterol are included because of the information yielded regarding the nature of the elastic effects.

THEORY

Some general aspects of the theory of surface viscosity measurement and an experimental comparison of the results obtained for long-chain normal alcohols by oscillating discs or rings and oscillating vanes have already been published (6). The theory of the oscillating-vane method

¹ The material of this paper is from the thesis presented by the author in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the School of Graduate Studies of Washington University. A preliminary description of this work has been published elsewhere (5).

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is less familiar than that for systems of circular symmetry presented by Langmuir and Schaefer (9) and is therefore outlined here.

Oberbeck (13) compared the rate of damping of the oscillations of a vane, according as it was completely immersed in a liquid or as its upper edge approached and penetrated the surface. In the present work the surface is penetrated by the lower edge of the vane only, so that the sensitivity to changes seated at the air-water interface is increased. The essential difference between this work and that of Oberbeck is in the recognition of the presence of a film, deliberately caused to be present and quantitatively specified by the film-balance technique of Langmuir, Adam, and Gorter.

Two conditions are postulated in the quantitative theory of the method: (1) that the differences between a clean surface and one covered with a film can be attributed entirely to the film, and (2) that the resistance of the film to an oscillating vane may be localized as rupture at the ends of the vane. The first assumption requires that any resistance of water accompanying the film be included in the computed film resistance, but this is only a magnification of an effect essentially caused by cohesion within the film itself. The effective immersion of the vane must remain the same in the presence of the film. For films of many substances the resistance rises to values a thousandfold greater than that of the clean surface.

The differential equation

$$I \frac{d^2\theta}{dt^2} + R \frac{d\theta}{dt} + \tau\theta = 0 \quad (1)$$

for the oscillation of a system with moment of inertia I , having a resisting torque $R \frac{d\theta}{dt}$ proportional to the angular velocity, and a restoring torque $\tau\theta$ proportional to the angular displacement θ , leads to the expressions

$$\frac{1}{P} = \frac{1}{2\pi} \sqrt{\frac{\tau}{I} - \frac{R^2}{4I^2}} \quad (2)$$

and

$$\lambda = \frac{RP}{2I} \quad (3)$$

in which P is the period and λ is the logarithmic decrement. According to the second condition, the torque $R \frac{d\theta}{dt}$ arises from the rupture of the film at the ends of the vane. It is convenient to obtain λ in common logarithms, 'converting to base e by the factor 2.3. The resistance of the clean surface is to be subtracted, according to the first condition. Letting

l be the length of the vane and σ the force in dynes required to rupture the film at unit rate, we have

$$\sigma = \Delta \left(\frac{\lambda_0}{P} \right) \frac{I}{l^2} 4 \times 2.3 \quad (4)$$

The quantity σ has the dimensions of surface viscosity, the unit being the "surface poise".

If the film has no appreciable elasticity, the effect of increasing cohesion of its molecules is to increase R , and hence lengthen P , according to equation 2. But if elastic forces in the film add to the restoring torque of the suspension, the value of τ is increased, hence shortening P . As a protein film is compressed, P is observed first to increase slightly, then to decrease greatly. These effects are illustrated in table 1 and in figure 2. The contribution, $\Delta\tau$, of the film to the restoring torque can be computed:

$$\Delta\tau = I \left(\frac{4\pi^2 + \lambda^2}{P^2} - \frac{4\pi^2 + \lambda_0^2}{P_0^2} \right) \quad (5)$$

The subscripts refer to the clean surface. A sufficiently accurate approximation in a form more convenient for calculation is obtained by neglecting the λ 's:

$$\Delta\tau = 4\pi^2 I \left(\frac{1}{P^2} - \frac{1}{P_0^2} \right) \quad (6)$$

A logical first assumption as to the nature of the elastic force exerted on the vane by the film is that it is compressional. This was the view of Marangoni (11), that the advancing vane piled up the film before it and left the water surface clean behind. However, one can have certain films (long-chain alcohols, cholesterol) under high pressure, without any elastic effects. To be manifest, a sweeping action would require either a very large viscosity or the presence of shear elasticity. The latter can be demonstrated in many films by the behavior of talc motes, and would itself contribute to the elastic effect.

A theoretical analysis of the elastic effect resulting in an expression for the elastic constants (compressibility, modulus in shear) has not yet been accomplished. Trials have led to the empirical result that the effect of change in the length of vane can be taken into account by computing an elasticity index:

$$E = \frac{\Delta\tau}{l^3} \quad (7)$$

This index can be used to compare and characterize films of different substances.

PROCEDURE

A film balance and trough of the Langmuir-Adam type furnished pressure-area data. Proteins were spread from solution by Gorter's technique. From 30 to 60 min. were allowed to insure relatively complete spreading before compression was begun. The stepwise compression of the film extended from 1 to 4 hr. In the pressure-area plots only the equilibrium points are shown; equilibration was not so extensive as that observed for egg albumin (7). Cholesterol was dissolved in redistilled benzene and applied dropwise. The trough was 14 cm. wide and 1.8 cm. deep. To obtain maximum symmetry, the oscillating vane was suspended 7 cm. in front of the float which divides the clean surface from that which is covered with film. A box with suitable doors and windows inclosed the apparatus, preventing disturbances from drafts.

The oscillating system was a brass cylinder, split in half along the axis and held together by brass screws. The phosphor bronze suspension wire was soldered into a small brass plug, which screwed into the center of the upper end of the cylinder. A microscope cover glass clamped symmetrically in the lower end of the cylinder served as the vane. The glass was cleaned with hot chromic-sulfuric acid before each experiment. A pair of air jets directed at the ends of the vane served to control oscillation in either direction. The lower edge of the vane should parallel the water surface, and in its resting position the vane should be parallel to the direction of compression. Under these conditions the vane suffers no displacement during the compression of a strongly coherent film, since the sharp edge can cut the film. At the same time, the vane acts like a screw-driver blade, and does not break loose from the film, as a circular object has frequently been observed to do (14, 15, 12). These considerations indicate the special applicability of the vane to highly rigid films. An oscillating ring system was not satisfactory for this type of film, because it showed a marked tendency to be carried along as the film (casein) was compressed. The moment of inertia in all of the experiments was 105 g. cm.²; the period in the clean surface was about 12.2 sec., except in some preliminary experiments in which it was 4.05 sec. Period and decrement were independent of amplitude, for the films studied here; any trend with amplitude was so slight as to be obscured by random variations. Hence five or ten swings were used whenever possible, to facilitate computation of λ_{10} . The average of two or three sets at a given area and pressure is presented as a single point.

MATERIALS

The cholesterol was from the Eastman Kodak Company (Rochester, New York). The casein was "Labco" brand, vitamin-free, from the Casein Corporation of America (New York City). Casein solutions were

made up by dissolving the powder in 0.1 *M* sodium hydroxide, then neutralizing the solution with acetic acid, the final solution being 0.01 *M* in sodium acetate, and containing about 1 mg. of casein per milliliter.

Nerve proteins were simple extracts of minced leg and claw nerves of lobsters in isotonic phosphate buffer, pH 7.4, clarified by centrifuging and filtering. This extract has been shown by Bear, Schmitt, and Young (3) to contain as its chief protein constituent the protein complex of the axis cylinder, designated by them as neuronin.

EXPERIMENTAL RESULTS

Cholesterol

Cholesterol is perfectly fluid to talc, as noted by Adam and Rosenheim (1). The period of the pendulum and the quotient, λ_{10}/P , which is proportional to the viscosity, show almost no change from the largest areas to the collapse of the film. The resistance is slightly less in the presence of the film than for the clean surface; in terms of viscosity the maximum decrease is 0.01 surface poise. This apparent negative viscosity is probably due to decrease of effective immersion of the vane combined with an extremely small viscosity.³ Decrease of surface tension lessens the capillary rise along the vane. This is borne out by an experiment with palmitic acid in which the vane was not quite level. At large surface pressures the higher end was released from contact with the water. The cholesterol experiment shows the independence of viscosity, and especially elasticity, from the film pressure, since the film was compressed to collapse without significant change.

Casein

The pressure-area graphs of five films are shown in figure 1. The uniformity of these films with respect to compression was the basis on which they were selected for testing equations 4 and 7. Other films, not so uniformly spread, showed similar relations.

Comparisons between the oscillating vane and talc observations were made in order to correlate the results with those of Hughes and Rideal (8), who noted the appearance of elasticity at a certain stage in the compression of gliadin films. Table 1 shows that the elasticity becomes apparent to talc at about the same step in compression as the first shortening of the period. That is, the vane method, as used here, has about the same sensitivity as the talc observation method, but has the advantage of permitting numerical comparison of degrees of elasticity.

In figure 2 are shown the data for the computation of elasticities and

³ Langmuir, Schaefer, and Sobotka (10) record the surface viscosity of cholesterol as less than 0.002 surface poise, the limit of sensitivity of their measurements.

viscosities. The open symbols represent results with a 5-cm. vane; the solid symbols are for a 3.5-cm. vane. Figure 3 shows the extent to which

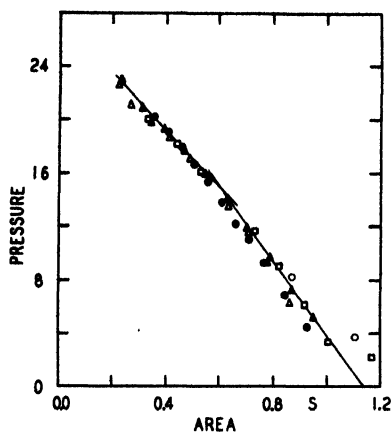


FIG. 1

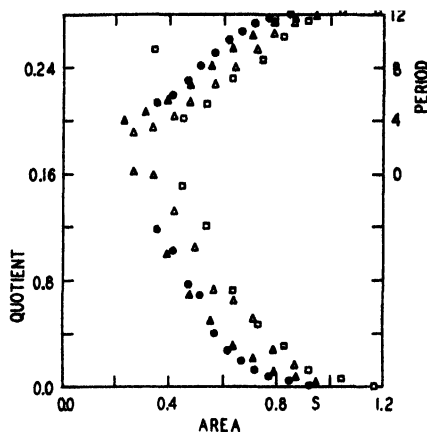


FIG. 2

FIG. 1. Pressure-area relations of casein on 0.01 *M* hydrochloric acid. Ordinate, surface pressure in dynes per centimeter; abscissa, area in square meters per milligram.

FIG. 2. Data from casein films for testing equations 4 and 7. Open symbols represent measurements with a vane 5.0 cm. long; solid symbols with a vane 3.5 cm. long. Ordinates: period in seconds, quotient λ_{10}/P . Abscissa, area in square meters per milligram.

TABLE 1

Comparison of observations with the vane and with talc

CASEIN	VANE IN					
	Air	Clean surface	Film			
			Talc indication			
			Fluid	Fluid	Resistant	Elastic
Labco casein:						
Period, in seconds	12.21	12.23	12.34	12.30	12.35	12.14
Decrement, λ_{10}	0.003	0.026	0.035	0.034	0.039	0.156
Area, m ² . per milligram			1.58	1.35	1.11	0.87
Pressure, dynes per centimeter			1.71	2.78	3.74	8.07
Crude casein:						
Period, in seconds	4.02	4.06	4.06	4.06	4.06	4.02
Decrement, λ_{10}	0.001	0.012	0.013	0.021	0.033	0.047

agreement is obtained between the viscosities measured with different vanes, using equation 4. This is taken as evidence favoring the validity of the equation. At low pressures the casein films are fluid; the point of

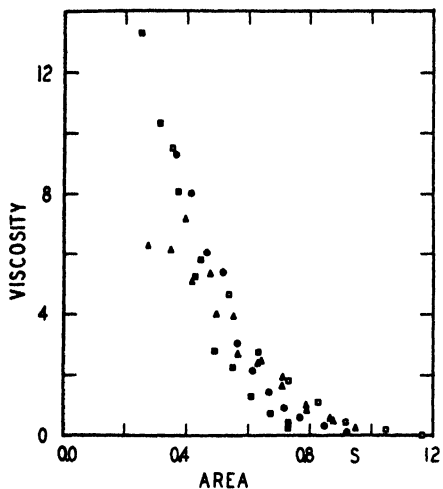


FIG. 3

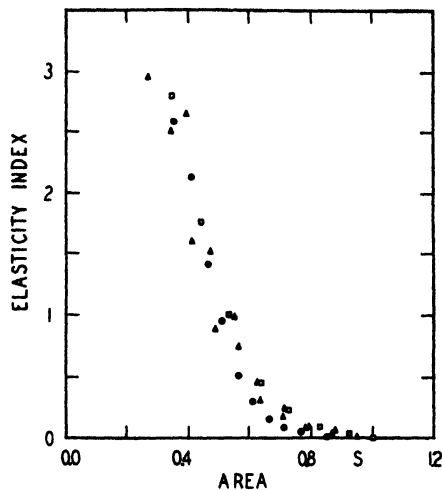


FIG. 4

FIG. 3. Viscosity of casein. The open and solid symbols represent measurements with vanes of different lengths brought to agreement by equation 4. Ordinate, viscosity in surface poises; abscissa, area in square meters per milligram.

FIG. 4. Elasticity of casein. The open and solid symbols represent measurements with vanes of different lengths brought to agreement by equation 7. Ordinate, elasticity index; abscissa, area in square meters per milligram.

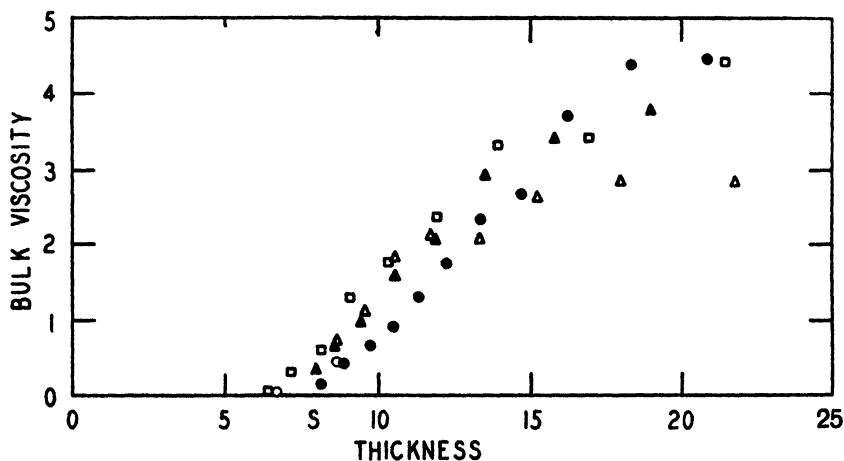


FIG. 5. Computed bulk viscosity of casein. The ordinate numbers times 10^7 are the viscosity in poises; the abscissa is the thickness of the film in Ångström units.

solidification, about 5 dynes and 0.95 square meter per milligram, is marked *S* in the figures. The elasticity index computed according to equation 7 is shown in figure 4.

Surface viscosity can be compared with bulk viscosity if we divide by the thickness of the film. In computing this, a density of 1.33, corresponding to the specific volume of protein in solution (4), was assumed for the material in the film. Figure 5 presents the results of this operation. The computed bulk viscosity is not constant, although a constant viscosity would be expected for increasing thicknesses of the same material, but increases, an indication that the structure of the film is different at each step in compression. The large magnitude of these viscosities rules out comparison with the viscosities of ordinary liquids. Since the films are in fact elastic solids, it is with the flow characteristics of solids that comparison should be sought.

Nerve proteins

A single preparation of nerve protein was used for all of the experiments at pH 5.0, another for those at pH 4.3, and two for those at pH 2.0. Data

TABLE 2
Spreading of nerve protein at pH 5.0

TRIAL	CONDITIONS	VOLUME OF SOLUTION	AREA OF FILM
		ml.	cm. ² per ml.
1	Aqueous protein solution on dilute buffer	0.1415	1230
2	Aqueous protein solution on dilute buffer	0.2885	1920
3	Alcoholic protein solution on dilute buffer	0.1400	4800
4	Alcoholic protein solution on dilute buffer	0.0852	4640
5	Aqueous protein solution on 0.5 M sodium chloride	0.1410	4600
6	Aqueous protein solution on 0.5 M sodium chloride	0.0650	4900

are lacking by which to compare the area relations between the different preparations, but for a particular preparation pressure-area comparisons in terms of area per milliliter of solution can be made. At each pH these relations had the general form shown by casein, that is, above the lowest pressures a straight line, intersected at a higher pressure by another straight line of lesser slope. Table 2 indicates the manner of spreading on 0.0033 M acetate buffer at pH 5.0. Applied directly, as in trials 1 and 2, the spreading was not quantitative, as the area (obtained by extrapolating the lower linear part of the plot to zero pressure) shows. However, by the addition of alcohol, diluting four volumes of nerve protein solution with one of 47.5 per cent alcohol, quantitative spreading was obtained. The same area was found for spreading at this pH on acetate buffer made 0.5 M in sodium chloride. The lower straight-line portion of the pressure-area curve began at about 2 dynes pressure; the intersection of the two linear parts came at 15 dynes per centimeter.

Another preparation of nerve protein showed a similar type of pressure-area relation on 0.0033 *M* acetate buffer at pH 4.3. Here the lower pressure-area line also began at about 2 dynes per centimeter; the intersection of the two linear portions at 20 dynes per centimeter. On 0.01 *M* hydrochloric acid, pH 2.0, only the first linear portion was observed, commencing at about 5 dynes per centimeter. The experiments only extended to 16 dynes per centimeter.

Figure 6 presents viscosity as a function of surface pressure for nerve protein on different subsolutions. This relation should be independent of

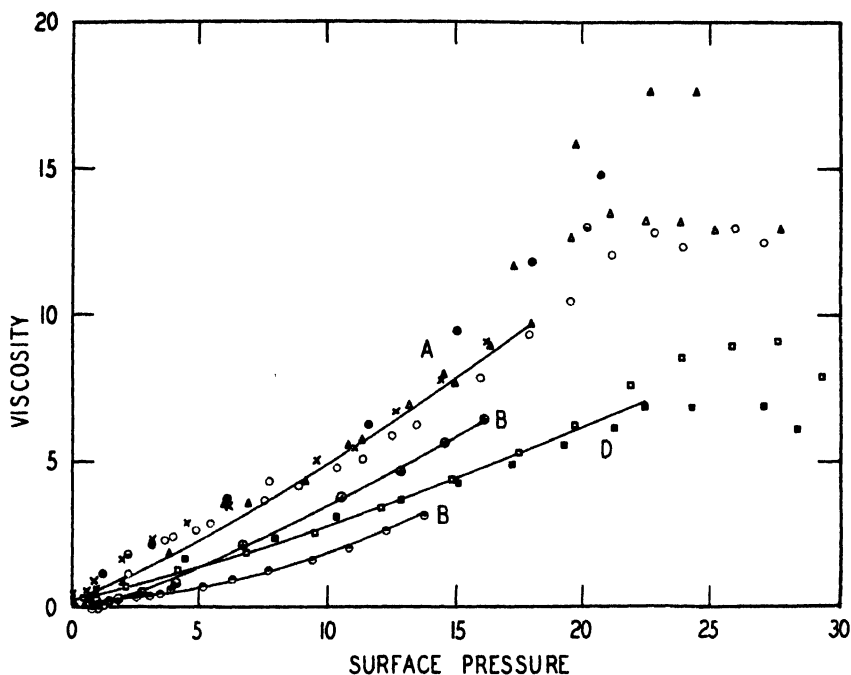


FIG. 6. Viscosity of nerve protein. Ordinate, viscosity in surface poises; abscissa, pressure in dynes per centimeter. Curves A, B, and D are for films on subsolutions of pH 5.0, 2.0, and 4.3, respectively.

the actual amount of protein on the surface. In curve A, which shows the values at pH 5.0, the results of trials 1 and 2 of table 2, in which spreading was incomplete, are represented by \times 's. Here, although all of the protein released did not go onto the surface, that which did is exactly like other films in which all of the protein was spread. This similarity is likewise shown by the elasticity relations presented in figure 7. The viscosity-surface pressure relations are nearly linear but show a slight upward curvature, continuing smoothly to pressures above that of the break between the two linear parts of the pressure-area curves.

On the subsolutions of pH 5.0 and 4.3 the films were elastic within a few seconds after spreading; even at zero pressure, with unoccupied surface available, they formed elastic membranes of definite shape. On acid solution, pH 2.0, however, the nerve protein resembled casein in remaining fluid at low pressures for several hours. On standing overnight under pressure on a solution of pH 2.0 the nerve protein underwent a change, in that upon reexpansion it was no longer fluid, but weakly elastic. This

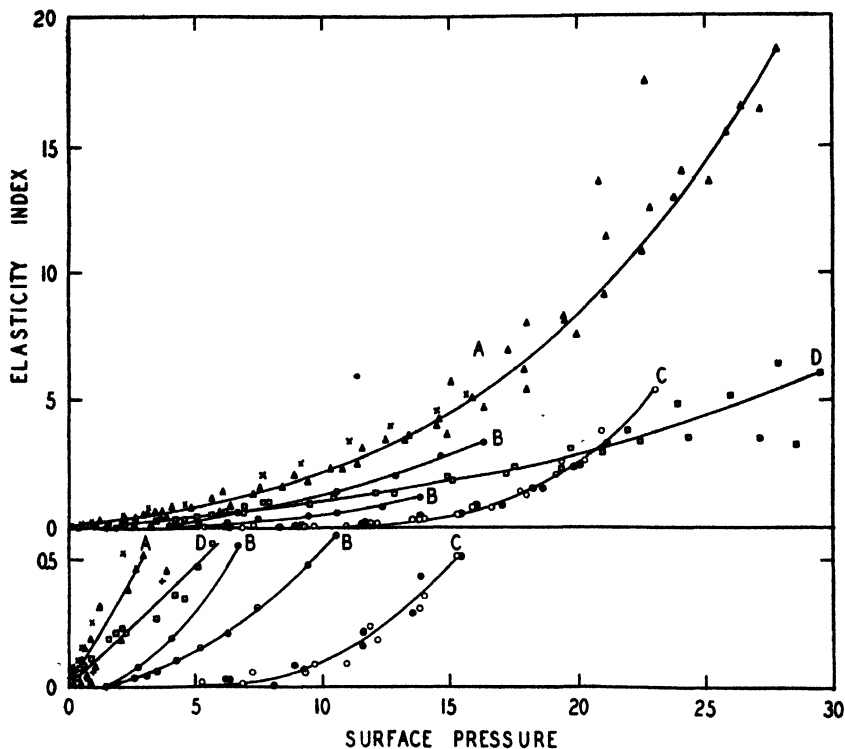


FIG. 7. Elasticity of protein films. Ordinate, elasticity index (on a tenfold larger scale in the lower portion); abscissa, pressure in dynes per centimeter. Curves A, B, and D are for nerve protein on subsolutions of pH 5.0, 2.0, and 4.3, respectively; curve C is for casein on 0.01 *M* hydrochloric acid. In curve C the open and solid symbols represent measurements with vanes of different lengths.

type of increase of elasticity with time was observed by Hughes and Rideal (8) with gliadin, and has been encountered with casein as well. This shows that the differences in elasticity at zero pressure are essentially differences in the rate of formation of bonds in the film. The elasticity indices of the films spread on subsolutions of different reactions are shown in figure 7. For these films from one-half to one hour of aging after spreading was allowed. The plot shows that on acid solution both casein and

nerve protein have vanishingly small elasticities at low pressures, while at the higher pH values the nerve protein has a marked elasticity down to the lowest pressures.

Although the nerve protein is knit together rapidly after spreading on solutions of pH 5.0 or 4.3, and shows elasticity even at zero pressure, there is an initial period in which the surface is mobile. This could be demonstrated by sprinkling the surface with talc before applying the protein, to make the film boundary visible. If the amount of protein and the area available for its spreading are so adjusted that some surface is always unoccupied, the patch of film is rounded, and this rounded outline is retained after the release of compression. However, if the film is spread on a restricted area, in which a pressure of a few dynes develops, and the barrier is then displaced to greater areas, the straight edge of the patch of film is retained. That is, during an early interval in which the film is fluid it can be moulded, after which it has a definite set.

DISCUSSION

Bonding of the protein molecules within the plane of the film, as evidenced by elasticity and viscosity, takes place either spontaneously with the passage of time or can be brought about by compression. For relatively short experiments of only a few hours duration, the elasticity and viscosity manifested upon compression are largely reversible. This suggests that the changes in elasticity and viscosity with compression arise rather simply from the felting together and mechanical interference of the separate protein molecules. The elasticity exhibited at zero pressure, whether soon after spreading or as a very slow development, seems better explained by relatively permanent bonds within the film. Presumptively these are of the same type as the labile bonds of native proteins.

It has been recognized, as pointed out by Cohn (4), that some kind of an unfolding must take place to account for the change of dimensions from the round shape of a dissolved protein molecule to the unimolecular film of much less thickness. The details of this unfolding are still a matter of speculation (see 2 and 16), but it is evident that the exposure of reactive groups capable of forming a plane polymer may be involved. The nature of these reactive groups should be revealed by the effects of substances dissolved in the subsolution upon the tendency of the film to form a membrane spontaneously. The pH dependence encountered here suggests that ionizable amino acid side chains are largely responsible; repression of carboxyl ionization by high acidity prevents intermolecular bridge formation, while at more nearly neutral reaction carboxyl groups of one molecule may unite with amino groups of another to form links between units.

This bonding of the protein to form an elastic membrane requires some time, even if the hydrogen-ion concentration is favorable. The initial

step of protein spreading is a fluid surface film. However, its condition need not be the same as the condition of the films that remain liquid a long time on acid solution. There the average thickness of the film, computed from area per milligram, implies an extensive change of molecular structure. In the first stage of spreading a film could be fluid with no change of molecular structure at all,—being in fact a thin layer of almost unchanged protein solution. For example, the average amount of protein solution used per film in these experiments was 0.08 ml., which would cover the area usually available (14 x 25 cm.) to the depth of 2×10^{-4} cm. This is 500 times the diameter, 40 Å., of a small protein molecule in solution.

The conception of the process of protein spreading as having two steps, (1) distribution as a layer of protein solution and (2) adsorption to the surface, with change of molecular shape and possible new linkage, permits an explanation of some of the methods of securing quantitative spreading. On acid solutions, or on others on which the film remains fluid, quantitative spreading is readily secured. Here the adsorption of a small amount of protein can bring about the distribution of the whole by forces conventionally described as surface tension. Although the adsorbed protein molecules are altered in structure and become insoluble, they are not bonded together and so offer no obstacle to continued spreading. When an elastic membrane is formed, however, it tends to restrain the distribution and prevent full spreading of the part of the protein solution last applied. Alcohol acts to prevent this by accelerating the first step,—distribution as solution. To some extent, the effect of increasing the electrolyte content of the subsolution may be the same, by increasing the surface tension difference. However, it is possible that the electrolyte may also act to favor adsorption of the protein to the surface, and promote spreading more by lowering the surface tension of the protein solution than by increasing that of the clean surface.

SUMMARY

1. The surface viscosity of unimolecular layers of proteins and other substances has been determined, subject to the fulfillment of certain conditions, from the damping of a vane oscillating in the film. This method is particularly useful in working with substances like proteins which form rigid films.

2. A quantitative index of surface elasticity is obtained from the shortening of the period of the oscillating vane. This effect is not due merely to the sweeping action of the vane but is related to the intrinsic elastic properties of the film materials.

3. Expressions relating the surface viscosity and elasticity to the length of the vane are given.

4. The pH of the subsolution is found to be an important factor in de-

termining the viscosity and elasticity of a protein film. The pH dependence of rapid bond formation within the film suggests that these links are ionic.

5. Quantitative spreading into the unimolecular film is observed when the processes which bring about distribution of the film substance precede or overbalance the restraining tendencies of rapid bond formation.

The author is much indebted to Professor F. O. Schmitt for aid and advice throughout the course of this work.

REFERENCES

- (1) ADAM, N. K., AND ROSENHEIM, O.: Proc. Roy. Soc. (London) **A126**, 25 (1929).
- (2) ASTBURY, W. T.: Nature **137**, 803 (1936).
- (3) BEAR, R. S., SCHMITT, F. O., AND YOUNG, J. Z.: Proc. Roy. Soc. (London) **B123**, 520 (1937).
- (4) COHN, E. J.: Ann. Rev. Biochem. **4**, 93 (1935).
- (5) FOURT, L.: Am. J. Physiol. **119**, 310 (1937).
- (6) FOURT, L., AND HARKINS, W. D.: J. Phys. Chem. **42**, 897 (1938).
- (7) FOURT, L., AND SCHMITT, F. O.: J. Phys. Chem. **40**, 989 (1936).
- (8) HUGHES, A. H., AND RIDEAL, E. K.: Proc. Roy. Soc. (London) **A137**, 62 (1932).
- (9) LANGMUIR, I., AND SCHAEFER, V. J.: J. Am. Chem. Soc. **59**, 2400 (1937).
- (10) LANGMUIR, I., SCHAEFER, V. J., AND SOBOTKA, H.: J. Am. Chem. Soc. **59**, 1751 (1937).
- (11) MARANGONI: Nuovo cimento [2] **5-6**, 239 (1872). Cited from Rayleigh (14).
- (12) MOQUIN, H., AND RIDEAL, E. K.: Proc. Roy. Soc. (London) **A114**, 690 (1927).
- (13) OBERBECK, A.: Weidemanns Annalen **11**, 534 (1880).
- (14) RAYLEIGH (STRUTT, J. W.): Scientific Papers **3**, 351, 363, Cambridge University Press; Proc. Roy. Institution **13**, 85 (1890); Proc. Roy. Soc. (London) **48**, 127 (1890).
- (15) SCHÜTT, K.: Ann. Physik [4] **13**, 712 (1904).
- (16) WRINCH, D. M.: Nature **137**, 411 (1936).

RAOULT'S LAW AND THE CLAPEYRON EQUATION FOR SUBSTANCES WHOSE VAPORS ARE POLYMERIZED

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For substances whose vapors consist of an equilibrium mixture of monomer and polymers, such as the carboxylic acids and hydrogen fluoride, it is known that a plot of the logarithm of the vapor pressure against the reciprocal of the absolute temperature is approximately a straight line, that to obtain an agreement between the measured heat of vaporization and that calculated from the Clausius-Clapeyron equation the calculated value must be taken for the apparent molecular weight in the vapor, and that for equations involving Raoult's law, such as those for molal boiling point rise or freezing point lowering, this same apparent molecular weight must be used.

In view of the complexity of the vapors it is surprising that Raoult's law in a simple form can be used and that the heat of vaporization per apparent molecular weight of vapor, as calculated from the Clapeyron equation, is approximately constant over a considerable temperature range. An explanation of these facts has sometimes been given on the assumption that the liquid consists of the same molecular species as the gas and in the same proportions. This assumption is obviously incorrect, as the high internal pressure in the liquid would certainly displace the equilibria in the direction of the higher polymers.

An analytical treatment of these problems is presented. This is accomplished without making any assumptions as to the nature of the liquid, the molecular species present in it, or its apparent molecular weight. In fact, it follows that these laws are powerless for investigation of the nature of the liquid.

THE VAPOR PRESSURE CURVE AND HEAT OF VAPORIZATION

Let us consider a liquid, A, whose vapor is composed of a monomer and $m - 1$ polymers of degree from 2 to m . If p_i is the partial pressure of A_i , its mole fraction in the vapor is p_i/P , where

$$P = \sum_1^m p_i \quad (1)$$

The heat L_i required to form 1 mole of A_i in the vapor from the liquid can be calculated from the equation

$$\frac{d \ln p_i}{d(1/T)} = \frac{-L_i}{R} \quad (2)$$

(assuming the perfect gas law for each species). L , the heat necessary to vaporize enough of the liquid to form 1 mole total of the vapor in equilibrium at pressure P , is then

$$L = \sum_i^m L_i \frac{p_i}{P} \quad (3)$$

Dividing by R , changing sign, and substituting from equations 2 and 1

$$\frac{-L}{R} = \frac{d \ln P}{d(1/T)} \quad (4)$$

The heat calculated from the vapor pressure curve is evidently that necessary to produce 1 mole total of the molecular species in the vapor at any particular temperature and at the pressure given by the vapor pressure at that temperature.

Let us now examine the conditions under which L will remain constant over a large range of temperature. If z is the apparent molecular weight of the vapor divided by the simple formula weight,

$$z = \sum_i^m \frac{i p_i}{P} \quad (5)$$

If ΔH_i is the heat of dissociation in the vapor from 1 mole of polymer, i , to the monomer,

$$L_i = iL_1 - \Delta H_i \quad (6)$$

In order to express L in terms of a given L_i and ΔH_i , either of two assumptions may be made. The vapor may consist of only two species in appreciable quantities, which is equivalent to the statement that one ΔH_i is large relative to all other ΔH_i 's, or the vapor may consist of many polymers but related in the way that chains of different lengths are related. In the latter case

$$\Delta H_i = (i - 1)\Delta H_2 \quad (7)$$

By the use of either of these assumptions and equations 5, 6, and 3,

$$L = zL_1 + \frac{1-z}{z} \Delta H_2 \quad (8)$$

From this it is easily found that the condition for L to remain constant over a temperature range neglecting the difference in heat capacity of reactants and products and its change with temperature is that

$$L = L_1 = \frac{\Delta H_i}{i - 1} \quad (9)$$

TABLE 1

Values of z for acetic acid and hydrogen fluoride

ACETIC ACID			HYDROGEN FLUORIDE		
Temperature	z at P (= vapor pressure)	Reference	Temperature	z at P (= vapor pressure)	Reference
°C.			°C.		
30	1.810	(6)	-55	3.98	(5)
40	1.783	(6)	-45	4.11	(5)
50	1.833	(8)	-39	4.37	(11)
60	1.792	(8)	-34.6	4.27	(5)
70	1.759	(8)	-21.5	4.17	(5)
80	1.733	(8)	-21	4.08	(11)
90	1.713	(8)	-12.4	3.87	(5)
100	1.698	(8)	-10	3.71	(11)
110	1.687	(8)	0 0	3.69	(5)
120	1.677	(8)	4.4	3.51	(5)
130	1.672	(8)	5.3	3.46	(11)

TABLE 2

*Values of $L_1 - (\Delta H_i/i)$ for four substances**

COMPOUND	L	APPARENT MOLECULAR WEIGHT	L		L_1	ΔH_i	$L_1 - \frac{H_i}{i}$
			Calculated	Experimental			
	<i>calories per mole</i>		<i>calories per gram</i>				
(HF) ₆ . . .	6150 (5)	64 (5, 11)	96	97 (10)	7,400	40,000 (11)	800
(CH ₃ COOH) ₂ .	9400 (8, 13)	101 (13)	93	97 (2)	12,200	16,400 (6)	4000
(HCOOH) ₂ . .	8280 (4)	72 (4)	114	116 (4)	10,400	14,000 (3)	3400
(NO ₂) ₂	8000 (7)	80 (12)	100	94 (1)	10,800	14,600 (12)	3500

* All values are at the normal boiling point. The numbers in parentheses are references to the literature.

When this is considered in connection with equation 4 and the fact that

$$\frac{d \ln K_i}{d(1/T)} = -\frac{\Delta H_i}{R} \quad (10)$$

it is seen that it is equivalent to the statement that z at a pressure of the vapor equal to the vapor pressure of the liquid is independent of tempera-

ture. In table 1 it is seen that this condition is approximately fulfilled for acetic acid and hydrogen fluoride.

If the same number and kinds of bonds are broken when a mole of monomer is formed from the surface of the liquid as when produced by dissociation of the polymer, L_1 should equal $\Delta H_i/i$. Values of $L_1 - (\Delta H_i/i)$ should represent the difference in heat content between the formation of a mole of monomer from the liquid surface and its formation from the polymer in the vapor. This should roughly correlate the energy preserving the liquid state per mole of monomer. In table 2 values of $L_1 - (\Delta H_i/i)$ are given for four substances. It is known that the surface tension of hydrogen fluoride (9) is relatively very small; this agrees, at least in principle, with this idea. Of course the values given here are the differences between numbers whose precision is not high.

RAOULT'S LAW

Let us consider the addition at constant temperature of a solute to a liquid whose vapor consists of m polymers in equilibrium. The activity, a_i , of the i^{th} polymer in the liquid may be defined in terms of the fugacity, f_i , of that polymer in the vapor.

$$a_i = \frac{f_i}{f_i^0} \quad (11)$$

If N_i is the mole fraction of the i^{th} polymer,

$$a_i = 1 \quad \text{when} \quad N_i = 1 \quad (12)$$

Let n_i be the number of moles of polymer i and n_s the number of moles of solute. The activity of the solute may be defined as

$$a_s = \frac{f_s}{f_s^0} \quad (13)$$

and

$$\frac{a_s}{n_s} = 1 \quad (14)$$

when $n_s = 0$. From the general equation of partial molal quantities,

$$\sum_{i=1}^{i=m} n_i \frac{d \ln a_i}{dn_s} + n_s \frac{d \ln a_s}{dn_s} = 0 \quad (15)$$

Let i and j designate the degrees of any two polymers in equilibrium. By the law of mass action,

$$K_{ij} = \frac{f_j^i}{f_i^j} \quad (16)$$

Differentiating equations 16 and 11 logarithmically we find that

$$\frac{d \ln a_i}{dn_s} = \frac{d \ln f_i}{dn_s} = \frac{i}{j} \frac{d \ln f_i}{dn_s} \quad (17)$$

If f , the total fugacity, is defined by

$$f = \sum_{i=1}^{i=m} f_i \quad (18)$$

it may be expressed in terms of f_i by substituting for f_i its value in equation 16.

$$f = \sum_{i=1}^{i=m} \frac{f_i^{1/j}}{K_i^{1/j}} \quad (19)$$

The change in f , may be found in terms of the change in f by differentiating equation 19, substituting for K_{ij} its value from equation 16, and rearranging.

$$\frac{d \ln f_i}{j dn_s} = \frac{1}{\sum_{i=1}^{i=m} i f_i} \frac{df}{dn_s} \quad (20)$$

By substituting for $d \ln a_i/dn_s$ in equation 15 its value in equation 17 and then equation 20, we find

$$\frac{\sum_{i=1}^{i=m} i n_i}{\sum_{i=1}^{i=m} i f_i} \frac{df}{dn_s} + n_s \frac{d \ln a_s}{dn_s} = 0 \quad (21)$$

If we accept the experimental fact that da_s/dn_s is finite when $n_s = 0$ and, since $a_s = kn_s$ when $n_s = 0$, for the addition of an infinitesimal amount of solute to the pure solvent, we find

$$\frac{da_s}{dn_s} = \frac{a_s}{n_s} = \text{constant} \quad (22)$$

As the second term of equation 21 becomes unity and since $dn_s = n_s$ for a sufficiently dilute solution,

$$\frac{df}{\sum_{i=1}^{i=m} i f_i} = - \frac{n_s}{\sum_{i=1}^{i=m} i n_i} \quad (23)$$

This may be simplified for the case where the fugacity of each polymer is related to its partial pressure in the vapor by the same proportionality constant.

$$\frac{df}{\sum_{i=1}^{i=m} if_i} = \frac{dP}{\sum_{i=1}^{i=m} ip_i} \quad (24)$$

From equations 5, 23, and 24

$$\frac{dP}{P} = -\frac{zn_s}{\sum_{i=1}^{i=m} in_i} \quad (25)$$

The very striking fact is now evident that the ratio dP/P is independent of the molecular species assumed to be present in the liquid, since

$$\sum_{i=1}^{i=m} in_i$$

is always equal to the total number of moles of monomer that could be obtained regardless of the extent of polymerization. The second term of equation 25 is equal to the mole fraction of solute, N_s , computed as though the liquid had the same molecular weight as its vapor, which for complex vapors is the apparent molecular weight. Hence

$$\frac{dP}{P} = -N_s \quad (26)$$

This equation has been derived for the limiting case in which the fugacity of each polymer is related to its pressure by the same proportionality constant. This, however, is to be expected, because of the inherent chemical similarity of the different polymers.

By combining the Clausius-Clapeyron equation (4) with the modified expression for Raoult's law (26), we finally arrive at exactly the same expression for the molal elevation of the boiling point which applies for non-polymerized substances.

$$K_b = \frac{RT^2}{L \frac{1000}{zM}} = \frac{RT^2}{l \ 1000} \quad (26)$$

(M = molecular weight of monomer; l = heat of vaporization per gram.)

If the assumption can be made that a liquid consists almost exclusively of one species of polymer, then some modification of Trouton's or similar rules and also of the law of corresponding states must be made. The boiling point must be taken as that temperature where the partial pressure of that polymer in the vapor is 1 atmosphere.

SUMMARY

Raoult's law and the Clapeyron equation have been considered for the case where the vapor of the substance consists of a monomer and any number of polymers. Raoult's law is shown to be independent of the nature of the liquid and to depend upon the determined apparent molecular weight of the vapor. It is simple in form and can be readily applied to equations for boiling point rise, etc. An explanation is given for the relatively straight line obtained when the logarithm of the vapor pressure is plotted against the reciprocal of the absolute temperature for substances such as acetic acid and hydrogen fluoride.

REFERENCES

- (1) BERTHELOT AND OGIER: *Ann. chim. phys.* **30**, 382 (1883).
- (2) BROWN: *J. Chem. Soc.* **83**, 987 (1903).
- (3) COOLIDGE: *J. Am. Chem. Soc.* **50**, 2166 (1928).
- (4) COOLIDGE: *J. Am. Chem. Soc.* **52**, 1874 (1930).
- (5) FREDENHAGEN: *Z. anorg. allgem. Chem.* **210**, 210 (1933).
- (6) MACDOUGALL: *J. Am. Chem. Soc.* **58**, 2585 (1936).
- (7) MITTASCH, KUSS, AND SCHLUETER: *Z. anorg. allgem. Chem.* **159**, 1 (1926).
- (8) RAMSAY AND YOUNG: *J. Chem. Soc.* **49**, 790 (1886).
- (9) SIMONS AND BOUKNIGHT: *J. Am. Chem. Soc.* **54**, 129 (1932).
- (10) SIMONS AND BOUKNIGHT: *J. Am. Chem. Soc.* **55**, 1458 (1933).
- (11) SIMONS AND HILDEBRAND: *J. Am. Chem. Soc.* **46**, 2183 (1924).
- (12) VERHOEK AND DANIELS: *J. Am. Chem. Soc.* **53**, 1250 (1931).
- (13) YOUNG: *J. Chem. Soc.* **59**, 903 (1891).

STUDIES ON AGING AND COPRECIPITATION. XXIX

THE AGING OF ORTHO FERRIC HYDROXIDE IN THE ABSENCE AND PRESENCE OF DIVALENT IONS IN AMMONIACAL MEDIUM¹

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In a previous study (2) from this laboratory it was shown that the adsorption of copper from ammoniacal medium on ortho ferric hydroxide decreased relatively slowly when the precipitate was aged in the presence of ammonia at room temperature and much more rapidly when the aging was carried out at 98°C. However, when the aging was carried out at room temperature in the presence of copper the amount of this ion removed from the solution increased very slowly, and much faster when the aging was carried out at 98°C.

In the present study the effect of various other divalent ions upon the aging of ortho ferric hydroxide has been investigated. For materials used and methods of analysis reference is made to a previous study (3).

EXPERIMENTAL

The precipitates were formed in the absence and presence of divalent ions at room temperature, and were aged in ammoniacal medium in the presence of divalent ions.

In general, the experiments were carried out in the following manner: (a) In the coprecipitation experiments the ammonia was added at room temperature to a mixture consisting of 25 ml. of 0.1 *M* ferric chloride, 25 ml. of approximately 0.08 *M* divalent ion, and the specified amount of ammonium chloride. The suspension was diluted to 100 ml. with distilled water, allowed to stand for the specified time at either room temperature or at 98°C., and filtered; the filtrate was analyzed. (b) In the adsorption experiments the ammonia was added to the ferric chloride solution at room temperature, the divalent ion was added immediately, and the suspension was then treated as in the coprecipitation experiments.

¹ This article is based upon a thesis submitted by L. G. Overholser to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1938.

The concentration of the divalent ion was approximately 0.02 *M* after diluting to 100 ml. Blanks were run which showed that it made no appreciable difference whether the suspension was shaken continuously or merely allowed to stand with occasional shaking. The experiments performed at 98°C. were carried out either in pressure flasks or in tightly stoppered 125-ml. Erlenmeyer flasks of Pyrex glass. Suitable blanks showed that no loss of ammonia or of the divalent ion occurred during the heating.

TABLE 1

Aging of ortho ferric hydroxide precipitated at room temperature in ammoniacal medium in the presence of zinc (approximately 0.02 M)

Ammonia concentration, 0.900 M

CONCENTRATION OF AMMONIUM CHLORIDE	TIME OF AGING	TEMPERATURE OF AGING	ADSORPTION OF ZINC		COPRECIPITATION OF ZINC	
			Zinc adsorbed	Zinc adsorbed per gram of Fe_2O_3	Zinc coprecipitated	Zinc coprecipitated per gram of Fe_2O_3
			per cent	millimoles	per cent	millimoles
<i>molar</i>						
0.077	7 min.	Room temperature			18.3	2.06
0.077	15 min.	Room temperature			17.6	1.98
0.077	40 min.	Room temperature	11.8	1.32		
0.077	1 hr.	Room temperature			16.4	1.84
0.077	12 hr.	Room temperature			16.1	1.81
0.077	2 days	Room temperature	13.0	1.46		
0.077	7 days	Room temperature	13.5	1.51	15.8	1.78
0.077	44 days	Room temperature	14.1	1.59	15.1	1.70
0.077	5 min.	98°C.			19.9	2.23
0.077	15 min.	98°C.			24.1	2.70
0.077	40 min.	98°C.	24.3	2.73		
0.077	1 hr.	98°C.			28.3	3.18
0.077	2 days	98°C.	47.1	5.28	52.4	5.88
1.75	11 min.	Room temperature			2.4	0.27
1.75	24 hr.	Room temperature			2.4	0.27
1.75	15 min.	98°C.			0	0
1.75	24 hr.	98°C.			0.8	0.08

Similar experiments were also carried out in 1.80 *M* ammonia and 0.077 *M* and 1.75 *M* ammonium chloride. The results were comparable to the above (see thesis of junior author).

In tables 1 to 5 the heading "adsorption" means that the divalent ion was added after the precipitation of the ferric hydroxide; "coprecipitation" denotes that the divalent ion was added prior to the precipitation.

In the case of manganese only a few short-time experiments were performed. In 0.003 *M* ammonia and 1.50 *M* ammonium chloride the adsorption after 8 hr. was practically unchanged (24.3 to 25.5 per cent); coprecipitation decreased from 28.5 to 26.7 per cent.

TABLE 2

Aging of ortho ferric hydroxide precipitated at room temperature in ammoniacal medium in the presence of nickel (approximately 0.02 M)

Concentration of ammonia, 0.900 M

CONCENTRATION OF AMMONIUM CHLORIDE	TIME OF AGING	TEMPERATURE OF AGING	ADSORPTION OF NICKEL		COPRECIPITATION OF NICKEL	
			Nickel adsorbed	Nickel adsorbed per gram of Fe_2O_3	Nickel coprecipitated	Nickel coprecipitated per gram of Fe_2O_3
<i>molar</i>			<i>per cent</i>	<i>millimoles</i>	<i>per cent</i>	<i>millimoles</i>
0.077	6 min.	Room temperature	9.4	0.93	14.3	1.43
0.077	1 hr.	Room temperature	11.5	1.14	14.8	1.47
0.077	1 day	Room temperature	12.9	1.29	15.1	1.50
0.077	7 days	Room temperature	13.6	1.36	15.8	1.57
0.077	30 days	Room temperature	14.7	1.47	15.8	1.58
0.077	30 min.	98°C.	36.0	3.60		
0.077	35 min.	98°C.			39.4	3.93
0.077	5 hr.	98°C.	54.1	5.40	51.1	5.09
2.00	30 min.	98°C.	1.3	0.13		
2.00	35 min.	98°C.			1.4	0.14
2.00	5 hr.	98°C.	2.2	0.21	1.8	0.18

TABLE 3

Aging of ortho ferric hydroxide precipitated at room temperature in ammoniacal medium in the presence of cobalt (approximately 0.02 M)

Concentration of ammonia, 0.900 M

CONCENTRATION OF AMMONIUM CHLORIDE	TIME OF AGING	TEMPERATURE OF AGING	ADSORPTION OF COBALT		COPRECIPITATION OF COBALT	
			Cobalt adsorbed	Cobalt adsorbed per gram of Fe_2O_3	Cobalt coprecipitated	Cobalt coprecipitated per gram of Fe_2O_3
<i>molar</i>			<i>per cent</i>	<i>millimoles</i>	<i>per cent</i>	<i>millimoles</i>
1.00	10 min.	Room temperature	11.0	1.12	17.4	1.78
1.00	40 min.	Room temperature	15.2	1.56	18.6	1.89
1.00	1 hr.	Room temperature	19.2	1.96	19.5	1.99
1.00	1 day	Room temperature	22.7	2.32	22.2	2.26
1.00	7 days	Room temperature	25.4	2.60	23.6	2.39
1.00	30 min.	98°C.	32.7	3.35	32.8	3.34
1.00	5 hr.	98°C.	56.0	5.73	58.5	5.95
2.00	40 min.	Room temperature	7.3	0.75	12.3	1.25
2.00	30 min.	98°C.	18.9	1.94	19.1	1.94
2.00	5 hr.	98°C.	33.0	3.38	34.4	3.48

TABLE 4

Aging of ortho ferric hydroxide precipitated at room temperature in ammoniacal medium in the presence of magnesium (approximately 0.02 M)

Concentration of ammonia, 0.900 M

CONCENTRATION OF AMMONIUM CHLORIDE	TIME OF AGING	TEMPERATURE OF AGING	ADSORPTION OF MAGNESIUM		COPRECIPITATION OF MAGNESIUM	
			Magnesium adsorbed	Magnesium adsorbed per gram of Fe_2O_3	Magnesium coprecipitated	Magnesium coprecipitated per gram of Fe_2O_3
<i>molar</i>			<i>per cent</i>	<i>millimoles</i>	<i>per cent</i>	<i>millimoles</i>
1.00	5 min.	Room temperature	10.6	1.12	15.1	1.57
1.00	1 hr.	Room temperature	12.2	1.30	16.0	1.67
1.00	7 days	Room temperature	14.9	1.59	16.0	1.67
1.00	40 min.	98°C.			13.9	1.45
1.00	2 hr.	98°C.			13.9	1.45
1.00	1 day	98°C.	13.0	1.38	12.1	1.26
2.00	10 min.	Room temperature			11.5	1.20
2.00	1 hr.	Room temperature			11.0	1.14
2.00	1 day	Room temperature			10.6	1.10
2.00	7 days	Room temperature			9.0	0.93

TABLE 5

Aging of ortho ferric hydroxide precipitated at room temperature in ammoniacal medium in the presence of calcium (approximately 0.02 M)

Concentration of ammonia, 0.900 M

CONCENTRATION OF AMMONIUM CHLORIDE	TIME OF AGING	TEMPERATURE OF AGING	ADSORPTION OF CALCIUM		COPRECIPITATION OF CALCIUM	
			Calcium adsorbed	Calcium adsorbed per gram of Fe_2O_3	Calcium coprecipitated	Calcium coprecipitated per gram of Fe_2O_3
<i>molar</i>			<i>per cent</i>	<i>millimoles</i>	<i>per cent</i>	<i>millimoles</i>
0.077	40 min.	Room temperature	19.0	1.90	20.8	2.07
0.077	3½ hr.	98°C.	0.4	0.04		
0.077	2½ hr.	98°C.			8.2	0.82
1.00	5 min.	Room temperature	12.2	1.22	12.9	1.29
1.00	1 hr.	Room temperature	12.7	1.27	12.9	1.29
1.00	7 days	Room temperature	10.7	1.06	10.6	1.05
1.00	3½ hr.	98°C.	2.0	0.20		
1.00	2½ hr.	98°C.			5.4	0.53

Coprecipitation at 98°C., followed by aging at 98°C.

In these experiments the mixture of ferric chloride and divalent metal was heated to 98°C., the ammonia added, the suspension diluted to 100 ml., aged at 98°C., filtered, etc.

In general, the results obtained were comparable to those obtained when coprecipitation was carried out at room temperature, though the rate of

increase of coprecipitation on aging at 98°C. was somewhat less for the precipitates formed at 98°C. than at room temperature. A few representative values for changes occurring on aging are listed: Zinc increased from 17.7 to 40.2 per cent after heating for 20 hr. in 0.900 *M* ammonia and 0.098 *M* ammonium chloride. Nickel increased from 18.7 to 34.9 per cent after heating for 30 min. in 0.900 *M* ammonia and 0.097 *M* ammonium chloride. Cobalt increased from 19.7 to 30.9 per cent after heating for

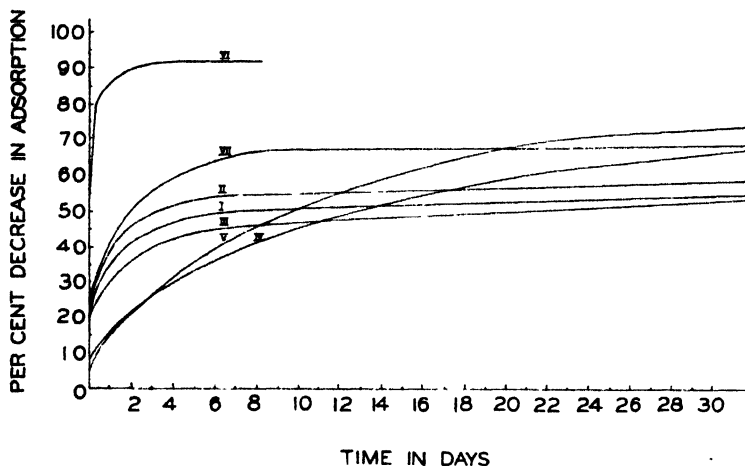


FIG. 1. Aging of ortho ferric hydroxide formed at room temperature in ammoniacal medium in the absence of divalent metal ions. The aging is measured by the decrease in adsorption of the divalent ions and of Niagara Sky Blue. Curve I, decrease in adsorption of zinc ion by ortho ferric hydroxide aged at room temperature in 0.090 *M* NH_3 + 0.103 *M* NH_4Cl ; curve II, decrease in adsorption of zinc ion by ortho ferric hydroxide aged at room temperature in 0.70 *M* NH_3 + 0.10 *M* NH_4Cl ; curve III, decrease in adsorption of nickel ion by ortho ferric hydroxide aged at room temperature in 0.005 *M* NH_3 + 0.08 *M* NH_4Cl ; curve IV, decrease in adsorption of methylene blue by ortho ferric hydroxide aged at room temperature in 1 *M* NH_3 + 0.1 *M* NH_4Cl ; curve V, decrease in adsorption of Niagara Sky Blue by ortho ferric hydroxide aged at room temperature in 1 *M* NH_3 + 0.1 *M* NH_4Cl ; curve VI, decrease in adsorption of zinc ion by ortho ferric hydroxide aged at 98°C. in 0.012 *M* NH_3 + 0.155 *M* NH_4Cl ; curve VII, decrease in adsorption of nickel ion by ortho ferric hydroxide aged at room temperature in 1.45 *M* NH_3 + 0.124 *M* NH_4Cl .

30 min. in 0.900 *M* ammonia and 1.00 *M* ammonium chloride. Magnesium showed very little change, increasing from 12.1 to 12.6 per cent after 2 hr. of heating in 0.900 *M* ammonia and 1.00 *M* ammonium chloride.

Aging of the ortho ferric hydroxide formed at room temperature in ammoniacal medium in the absence of divalent metal ions

In these experiments the ammonia was added to the ferric chloride at room temperature, following which the precipitate was allowed to age in solutions of ammonia and ammonium chloride of specified concentrations

for various periods of time at either room temperature or 98°C. At the end of the aging period, the divalent ion was added, the suspension made up to 100 ml., shaken for 40 min., filtered, and the filtrate analyzed. The results are given in figure 1, in which the aging is represented by the percentage decrease in the adsorption of the divalent ions. The aging as measured by the adsorption of an acid dye, Niagara Sky Blue, is also included.

Experiments on ferrite formation

The large amounts of zinc, nickel, and cobalt removed from solution during the aging of the ortho ferric hydroxide at 98°C. in ammoniacal medium in the presence of these metals suggested that some compound such as a ferrite was formed. Ferrites of the general formula $\text{MeO} \cdot \text{Fe}_2\text{O}_3$ of the above metals have been prepared, although no reference is made to their formation in ammoniacal solution. To determine whether or not such ferrites could be formed in ammoniacal medium, a number of experiments were performed in which the ortho ferric hydroxide was heated at 98°C. for various periods of time and with different concentrations of zinc and nickel. Equilibrium was never attained, the molecular ratio of MeO to Fe_2O_3 increasing with the time of heating and also increasing with increasing concentrations of the metals. Products were obtained in which the molecular ratio of zinc oxide to ferric oxide ranged from 0.92 to 2.53, and that for nickel oxide from 1.05 to 2.23. These results would show that no simple compound of the type $\text{MeO} \cdot \text{Fe}_2\text{O}_3$ was formed; probably either a ferrite of more complex composition results, or zinc oxide and nickel oxide form solid solutions with ferric oxide. Since the heating was carried out in Pyrex glass flasks one product was analyzed for silica. The precipitate was found to contain 1.28 millimoles of Fe_2O_3 , 1.02 millimoles of NiO , and only 0.05 millimole of SiO_2 . The small amount of silica found shows conclusively that the large amount of nickel oxide in the precipitate cannot be attributed to the formation of some complex silicate.

Aging of the ortho ferric hydroxide as indicated by dye adsorption

The aging of the ortho ferric hydroxide in ammoniacal medium was studied by determining the adsorption of an acid dye, Niagara Sky Blue, and a basic dye, methylene blue. The former was a purified product used in a previous study (5); the latter a product of high purity from the National Aniline and Chemical Company. Aqueous solutions of the dyes containing 1 g. per liter were used as stock solutions. All experiments with methylene blue were performed in paraffined bottles provided with paraffined cork stoppers to avoid adsorption of the dye by the glass. This precaution was not necessary in the experiments with Niagara Sky Blue.

The dye concentration of the respective solutions was determined by

means of the Lange photoelectric colorimeter. Because of the intense color of the dye solutions, it was necessary to use a low concentration of dye in the measurements (0 to 3 mg. per liter). In the case of Niagara Sky Blue, Beer's law was obeyed up to a concentration of 3 mg. per liter, but the results deviated greatly from it thereafter. A variation of the pH had a slight effect on the readings, necessitating the preparation of the standards in the same environment as the unknowns. Methylene blue did not obey Beer's law even at low concentrations, so that the use of an empirical curve was required. The absorption by methylene blue was not affected by changes in pH, if the pH was greater than 3.

Since the amount of dye adsorbed by the ortho ferric hydroxide depends on the pH of the solution (1), all experiments were performed in buffered solutions of known pH. The buffer solutions used were as follows:

pH of 5:	25 ml. of 0.4 M NH_3 + 39.28 ml. of 0.4 M CH_3COOH
pH of 6:	25 ml. of 0.4 M NH_3 + 26.43 ml. of 0.4 M CH_3COOH
pH of 7:	10 ml. of 0.4 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$
pH of 8:	26.43 ml. of 0.4 M NH_3 + 25 ml. of 0.4 M CH_3COOH
pH of 9:	39.28 ml. of 0.4 M NH_3 + 25 ml. of 0.4 M CH_3COOH
pH of 10:	35 ml. of 1.624 M NH_3 + 10 ml. of 1 M NH_4Cl

Preliminary dye experiments

In general, the specified volume of the above buffer solutions was introduced into a 100-ml. volumetric flask, 5 ml. of a suspension of ortho ferric hydroxide and the required volume of dye solution (containing 1 g. of dye per liter) were then added, and distilled water to make the volume 100 ml. The suspension was allowed to stand with occasional shaking for 1 hr., and centrifuged. Ten-milliliter samples were pipetted off and diluted to 1 liter with distilled water. It was found to make no difference whether the suspensions were shaken mechanically or occasionally. After 24 hr. of standing or shaking the adsorption of both dyes was relatively 3 per cent greater than after 1 hr.

Effect of pH

The adsorption of Niagara Sky Blue and methylene blue was determined at various pH values, using an initial dye concentration of 200 mg. per liter. The results are given in table 6.

The adsorption of Niagara Sky Blue attained a limiting value at a pH of approximately 6 and became negligibly small at a pH of 9, indicating that the isoelectric point of the hydroxide might be near the latter value. The adsorption of methylene blue suddenly increased to an almost constant value when the pH became greater than 10. The latter behavior is due not to the effect of pH upon the adsorption but rather to a replacing cation effect, as shown in the following section.

Cation effect upon adsorption of methylene blue

The adsorption of methylene blue, using an original dye concentration of 200 mg. per liter, was determined in 0.1 *M* ammonia and in the latter containing different concentrations of various salts. It was also determined in some buffers at different dilutions of the latter. The results,

TABLE 6
Adsorption of dyes by ortho ferric hydroxide

MEDIUM	pH	ADSORPTION OF NIAGARA SKY BLUE		ADSORPTION OF METHYLENE BLUE	
		mg.	per cent	mg.	per cent
Buffer	5	10.0	50.0	0	0
Buffer	6	10.0	50.0	(0.20)	(1.0)
Buffer	7	8.7	43.5	0	0
Buffer	8	3.9	21.5	0.50	2.5
Buffer	9	1.3	6.5	0.22	1.1
Buffer	10			0.80	4.0
0.04 <i>M</i> NH ₃	10.9			5.84	29.2
0.1 <i>M</i> NH ₃	11.1			6.03	30.1
0.2 <i>M</i> NH ₃	11.3			6.23	31.1
0.01 <i>M</i> NaOH	12.0			7.00	35.0
0.04 <i>M</i> NaOH	12.6			6.52	32.6

TABLE 7
Effect of cations on adsorption of methylene blue

	ADSORPTION	
	mg.	per cent
0.1 <i>M</i> NH ₃	5.39	26.9
0.1 <i>M</i> NH ₃ + 0.1 <i>M</i> NH ₄ Cl	0.13	0.6
0.1 <i>M</i> NH ₃ + 0.1 <i>M</i> KCl	1.79	8.9
0.1 <i>M</i> NH ₃ + 0.1 <i>M</i> NaCl	1.49	7.4
0.1 <i>M</i> NH ₃ + 0.01 <i>M</i> NaCl	5.00	25.0
1.0 <i>M</i> NH ₃ + 0.1 <i>M</i> NH ₄ Cl	0.52	2.6
0.1 <i>M</i> NH ₃ + 0.01 <i>M</i> NH ₄ Cl	3.25	16.2
0.01 <i>M</i> NH ₃ + 0.001 <i>M</i> NH ₄ Cl	3.93	19.7
0.01 <i>M</i> NaHCO ₃ + 0.045 <i>M</i> Na ₂ CO ₃	2.66	13.3
0.001 <i>M</i> NaHCO ₃ + 0.0045 <i>M</i> Na ₂ CO ₃	4.71	23.5
0.06 <i>M</i> NaHCO ₃ + 0.02 <i>M</i> Na ₂ CO ₃	2.96	14.8
0.006 <i>M</i> NaHCO ₃ + 0.002 <i>M</i> Na ₂ CO ₃	4.32	21.6

given in table 7, show the marked effect of salts such as sodium chloride in reducing the adsorption. Naturally, ammonium salts had a greater effect, as they changed the pH of the medium and in addition exerted a replacing effect upon the adsorbed methylene blue cation.

The adsorption of Niagara Sky Blue was not measurably affected by

salts. The presence of 0.1 *M* sodium chloride or a dilution of the different buffer solutions had very little, if any, effect.

Effect of dye concentration

The adsorption of Niagara Sky Blue was determined at a pH of 6 at different dye concentrations. Constant values for the adsorption were found with a final dye concentration of 100 mg. per liter and greater.

Effect of washing and centrifuging

A suspension of ortho ferric hydroxide was washed three times with water by centrifugation and siphoning off the supernatant liquid. The amount of Niagara Sky Blue adsorbed by the product at a pH of 6 and a final dye concentration of 100 mg. per liter was found to be 47.1 per cent, compared to 50 per cent for an unwashed product. When washed with a buffer of pH equal to 6 instead of water, a value of 48.8 per cent was found. Although the washing and centrifuging had a slight effect on the adsorption, it was not sufficiently great to prohibit the use of these operations in the subsequent experiments.

Short-time aging in the presence and absence of zinc

In some of the aging experiments the dye adsorption was determined after the hydroxide had been in contact with a zinc salt solution. In order to test the effect of small amounts of zinc on the adsorption of the dye, the following experiments were run: One sample of the ferric hydroxide was aged for 40 min. at room temperature in a medium which was 0.1 *M* in ammonium chloride, 1 *M* in ammonia, and 0.02 *M* in zinc sulfate. Another sample was similarly treated in a medium of 0.1 *M* ammonium chloride and 1 *M* ammonia. After the aging the precipitates were washed twice with a buffer of pH 6 and then with water. The adsorption of Niagara Sky Blue and methylene blue at original dye concentrations of 300 and 200 mg. per liter and at pH values of 6 and 11.1, respectively, was then determined on the products as well as on an unaged product. For Niagara Sky Blue the adsorption was found to be 35 per cent for the unaged product, 31.5 per cent for the one aged in the presence of zinc, and 30.9 per cent for the one aged in the absence of zinc. The corresponding values for methylene blue were 33.2, 30.8, and 29.9 per cent. These results show that standing for a short time in the presence of zinc had very little effect. Aging occurred in both instances, but most of it may have taken place during the washing process.

Aging of the ortho ferric hydroxide precipitated at room temperature in different media at room temperature and at 98°C.

The procedure used in the experiments was as follows: 312 ml. of 0.1 *M* ferric chloride was precipitated at room temperature by the addition of

9.6 ml. of 9.70 *M* ammonia. The precipitate was washed chloride-free by centrifugation and decantation and then suspended in a volume of 500

TABLE 8
Aging of ortho ferric hydroxide formed at room temperature

CONDITIONS OF AGING			ADSORPTION OF DYE PER GRAM OF Fe_2O_3		PERCENTAGE DECREASE IN THE ADSORPTION		RATIO OF N.S.B. TO M.B. AD-SORBED
Medium	Time	Temperature	N.S.B.*	M.B.	N.S.B.	M.B.	
			mg.	mg.	per cent	per cent	
50-min. old product			441	279			1.58
Water.	41 hr.	R.T.†	400	239	9.3	14.3	1.67
	9 days	R.T.	356	231	19.3	17.2	1.54
	30 days	R.T.	348	226	21.1	19.4	1.54
	1 hr.	98°C.	257	187	32.5	25.5	1.37
0.1 <i>M</i> NH_3	41 hr.	R.T.	378	231	14.3	17.2	1.64
	9 days	R.T.	319	214	27.8	23.3	1.49
	30 days	R.T.	270	171	38.9	38.7	1.58
	1 hr.	98°C.	213	160	44.1	36.2	1.39
1 <i>M</i> NH_3	41 hr.	R.T.	338	202	23.4	27.6	1.67
	9 days	R.T.	200	124	54.6	55.7	1.61
	30 days	R.T.	20	26	95.5	90.8	0.77
	1 hr.	98°C.	191	141	50.0	44.3	1.35
0.01 <i>M</i> NaOH	41 hr.	R.T.	324	202	26.2	27.6	1.60
	9 days	R.T.	143	108	67.5	61.2	1.32
	30 days	R.T.	64	34	85.5	87.9	1.87
	1 hr.	98°C.	143	151	62.4	39.8	0.95
1 <i>M</i> NH_3 + 0.1 <i>M</i> NH_4Cl	40 min.	R.T.	390	251	11.6	10.0	1.55
	41 hr.	R.T.	360	222	18.4	20.4	1.63
	9 days	R.T.	229	161	48.1	42.3	1.43
	30 days	R.T.	118	92	73.3	67.2	1.29
	1 hr.	98°C.	151	151	60.4	39.8	1.00
1 <i>M</i> NH_3 + 0.1 <i>M</i> NH_4Cl + 0.02 <i>M</i> ZnSO_4	40 min.	R.T.	397	259	10.0	7.2	1.53
	41 hr.	R.T.	378	251	14.3	10.0	1.51
	9 days	R.T.	336	237	23.8	15.0	1.40
	30 days	R.T.	336	231	23.8	17.3	1.41
	1 hr.	98°C.	232	171	39.2	31.8	1.36

* N.S.B. = Niagara Sky Blue; M.B. = methylene blue.

† Room temperature.

ml. of distilled water. Five-milliliter portions of this suspension were aged at room temperature and at 98°C. for definite periods of time in

different media. After the aging period, the supernatant liquid was removed; the precipitate was washed with a buffer having a pH of 6 and finally with water. The adsorption of methylene blue and of Niagara Sky Blue was then determined in the manner previously described. The former was carried out in 0.1 *M* ammonia with an original dye concentration of 200 mg. per liter, the latter in a buffer of pH equal to 6 and with a dye concentration of 300 mg. per liter. Five milliliters of the suspension contained 0.0238 g. of Fe_2O_3 .

The results are given in table 8, in which the adsorption of the two dyes after the aging at both temperatures is compared. The extent of the aging, as shown by the decrease in the adsorption of the dyes, is included and also

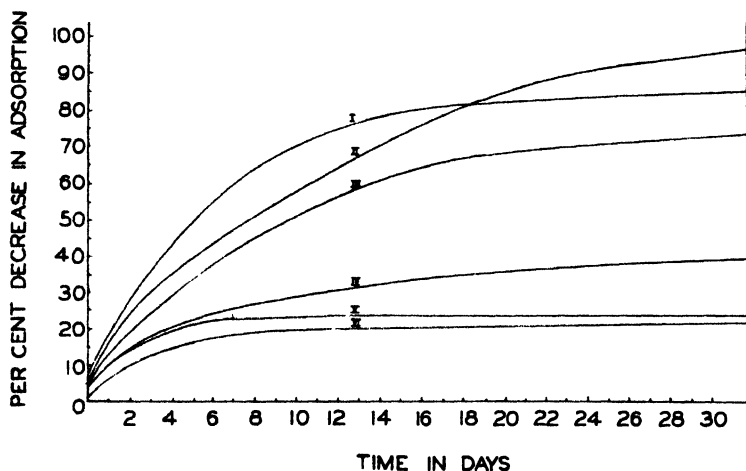


FIG. 2. Aging of ortho ferric hydroxide as measured by decrease of adsorption of Niagara Sky Blue. Curve I, aged in 0.01 *M* NaOH; curve II, aged in 1 *M* NH_3 ; curve III, aged in 1 *M* NH_3 + 0.1 *M* NH_4Cl ; curve IV, aged in 0.1 *M* NH_3 ; curve V, aged in 1 *M* NH_3 + 0.1 *M* NH_4Cl + 0.02 *M* ZnSO_4 ; curve VI, aged in water.

plotted in figure 2. The ratio of the amount of Niagara Sky Blue to that of methylene blue adsorbed is also included.

Dye adsorption on the ortho ferric hydroxide formed at 98°C.

A mixture consisting of 130 ml. of 0.1 *M* ferric chloride and 2.5 ml. of 6 *M* hydrochloric acid was heated to 98°C., and 10 ml. of 9.70 *M* ammonia was added. The suspension was cooled immediately, washed chloride-free, and suspended in 200 ml. of water. Ten-milliliter portions containing 0.052 g. of Fe_2O_3 were employed in the dye adsorption experiments, which were carried out in the same manner as the preceding ones. It was found that the amount of Niagara Sky Blue adsorbed per gram of Fe_2O_3 was 263 mg., compared to 441 mg. for a product formed at room tempera-

ture. The corresponding values for methylene blue were 146 and 279 mg., respectively.

DISCUSSION

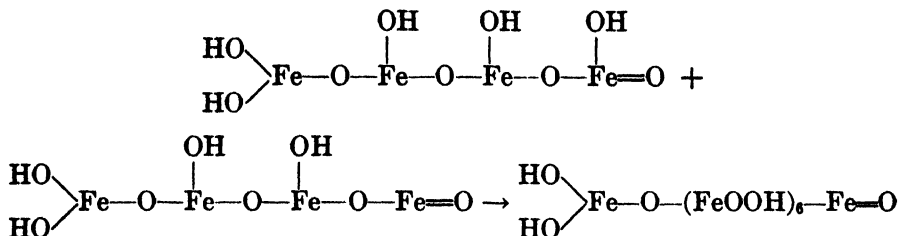
An examination of the results reported in tables 1 to 5 reveals that the adsorption of zinc increased slowly at room temperature on aging, whereas the coprecipitation showed a small decrease. On aging at 98°C. at a low ammonium chloride concentration, the increase of both the adsorption and coprecipitation was remarkably rapid. At a high ammonium chloride concentration, little change was noted when the aging was carried out at 98°C. In the case of nickel, both the adsorption and the coprecipitation increased rather slowly at room temperature, but again a very rapid increase was found when the aging took place at 98°C. at a low ammonium chloride concentration. The results with cobalt show a rapid increase of coprecipitation on aging at 98°C., even at a high ammonium chloride concentration. The values for magnesium changed very little on aging at either temperature. The adsorption and coprecipitation of calcium, on the other hand, decreased slightly on aging at room temperature and rapidly at 98°C.

From the results in table 8 it is quite evident that the adsorbed divalent metals inhibit the aging of ortho ferric hydroxide at room temperature, but they do not prevent the aging. In addition it was noticed that the color of the fresh precipitate, which was dark brown, changed to a yellowish brown after aging for about a week or 10 days in ammoniacal medium. When the precipitate was aged at room temperature in the same medium containing zinc, no visible change of color was detectable even after 44 days. At 98°C. the aging was also inhibited by adsorbed divalent metals, although not as effectively as at room temperature.

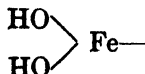
The increase in the adsorption and coprecipitation, particularly at 98°C., has to be explained by a chemical interaction between the adsorbed divalent metal oxide and the ferric oxide. The tendency to form ferrites decreases in the order cobalt, nickel, and zinc. Under the experimental conditions used, magnesium does not seem to have a tendency to form a ferrite, although the adsorbed magnesium inhibits the aging of the precipitate both at room temperature and at 98°C. Calcium behaved differently from the other cations; on aging at room temperature a slight desorption occurred and a very marked one on aging at 98°C. Apparently the adsorbed calcium hardly inhibits the aging of the ferric hydroxide.

When ortho ferric hydroxide was aged in the absence of divalent metal ions, the speed of aging was found to increase with increasing hydroxide-ion concentration of the solution (figures 1 and 2, table 8). The rate of decrease of the surface was found to be greatest during the early stages of aging.

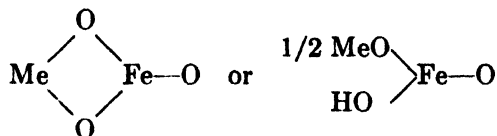
Krause and his coworkers (4) consider the aging of the ortho ferric hydroxide as a polymerization process. During the early stages of aging two molecules of the hydroxide react to form a polymerization product containing eight atoms of iron.



The chain can grow by the addition of more molecules of ortho ferric hydroxide until an agglomerate containing forty to fifty atoms of iron is formed. According to this view the



group plays an active part in the polymerization process. The inhibiting effect of adsorbed divalent metals then might be attributed to the formation of complexes of the nature



by which the group active in the polymerization is made inactive.

SUMMARY

1. When ortho ferric hydroxide formed at room temperature was aged in ammoniacal medium in the presence of zinc, nickel, or cobalt, the amount of metal removed from solution increased slowly on standing at room temperature and rapidly when the hydroxide was aged at 98°C. at a low ammonium chloride concentration. The increase is attributed to formation of a ferrite. When the ortho ferric hydroxide was aged in the presence of magnesium, little change was found in the amount of magnesium removed from solution at either temperature. Aging in the presence of calcium resulted in a slow decrease in the amount of calcium adsorbed at room temperature, but aging at 98°C. gave a rapid desorption.

2. Aging of the ortho ferric hydroxide in the absence of the metals resulted in a decrease in the adsorptive properties of the precipitate, as shown by a decrease in the amounts of divalent metal ions and dye adsorbed. The rate of this aging depended on the hydroxide-ion concentra-

tion. The aging was extremely slow in distilled water, more rapid in 1 *M* ammonia, and most rapid in 0.01 *M* sodium hydroxide. The rate of aging at 98°C. was found to be much greater than at room temperature.

3. The aging of ortho ferric hydroxide was inhibited by the presence of zinc, nickel, cobalt, and magnesium in ammoniacal medium. The inhibiting effect is attributed to a blocking of the hydroxyl group in the polymerization of the ferric hydroxide. Calcium did not exhibit this inhibiting effect.

4. Precipitates containing large amounts of zinc and nickel have been prepared. In some instances the ratio of $\text{MeO}:\text{Fe}_2\text{O}_3$ exceeded 2:1.

5. The adsorption of an acid dye, Niagara Sky Blue, and a basic dye, methylene blue, has been determined at various pH values. The amount of acid dye adsorbed increased with decreasing pH values, while the basic dye gave a reverse effect. It has been found that alkali ions repress the adsorption of the methylene blue cation.

REFERENCES

- (1) HÜTTIG, G. F., AND PETER, A.: *Kolloid-Z.* **54**, 140 (1931).
- (2) KOLTHOFF, I. M., AND MOSKOVITZ, B.: *J. Phys. Chem.* **41**, 629 (1937).
- (3) KOLTHOFF, I. M., AND OVERHOLSER, L. G.: *J. Phys. Chem.* **43**, 767 (1939).
- (4) KRAUSE, A.: *Z. anorg. allgem. Chem.* **176**, 398 (1928).
KRAUSE, A., AND CIOKÓWNA, M.: *Z. anorg. allgem. Chem.* **204**, 20 (1932).
KRAUSE, A., AND COLLABORATORS: *Z. anorg. allgem. Chem.* **204**, 386 (1932);
206, 328 (1932); **211**, 98 (1933); **219**, 213 (1934); *Kolloid-Z.* **72**, 18 (1935).
- (5) OVERHOLSER, L. G.: M. A. Thesis, University of Minnesota, 1935.

SOL AND GEL IN HEVEA LATEX AND CRUDE RUBBER¹

INFLUENCE OF OXIDATION ON GEL-SOL TRANSFORMATION

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From the work of Caspari (1), Feuchter (2), and others it is now well known that a large proportion of the hydrocarbon in unmasticated crude Hevea rubber diffuses into and is therefore soluble in petroleum ether or ethyl ether when the rubber is covered with these solvents and allowed to stand at room temperature.

This soluble form of rubber has been termed "sol," and the residue from a prolonged and repeated solvent extraction is known as the gel skeleton, which contains practically all of the protein and ash of the original rubber associated with the tough and gristly rubber hydrocarbon termed "gel." It is apparent that the terms "sol" and "gel" rubber are somewhat indefinite, as they do not refer to definite fractions or to rubber having definite physical or chemical characteristics.

From a purely colloidal viewpoint and by definition all rubber soluble by diffusion into a solvent is sol. However, we must recognize the indistinct borderline between difficultly soluble sol and almost insoluble gel.

The so-called sol rubber carefully prepared from acetone-extracted crepe by diffusion into petroleum ether forms a clear, colorless, and highly elastic substance upon evaporation of the solvent. It is almost pure hydrocarbon², since it contains less than 0.005 per cent nitrogen and 0.01 per cent ash. Its unsaturation, as determined from its iodine value (3), corresponds closely to the theoretical value for $(C_5H_8=)_n$.

Up to the present time studies of sol and gel rubber have been largely qualitative and confined to crude rubber and to highly purified rubber from latex. This paper will describe a definite procedure designed to determine the proportion of sol and gel in crude rubber and in dried latex films by the use of a petroleum ether diffusion process. The influence of oxidation on the transformation of gel to sol has been studied by the use of this method. A search of the literature indicates that this field has not been previously investigated.

¹ Presented before the Division of Rubber Chemistry at the Ninety-seventh Meeting of the American Chemical Society, held in Baltimore, Maryland, April 3-7, 1939.

² Midgley (5) found from 0.02 to 0.04 per cent of combined oxygen in sol rubber.

EXPERIMENTAL PROCEDURE

Fresh shipments of normal ammonia-preserved latex obtained in sealed cans from two sources were studied. Latex A was shipped from the East in tank ships and drummed on arrival, while latex B was shipped in drums directly from the plantation.

The solvent employed was petroleum ether, b. p. 35–58°C., and the extraction temperature ranged from 20° to 25°C. The ratio of solvent to sample was kept between 3.4 and 3.8 g. of rubber to 250 cc. of solvent. Petroleum ether is preferred to ethyl ether, since it does not contain per-

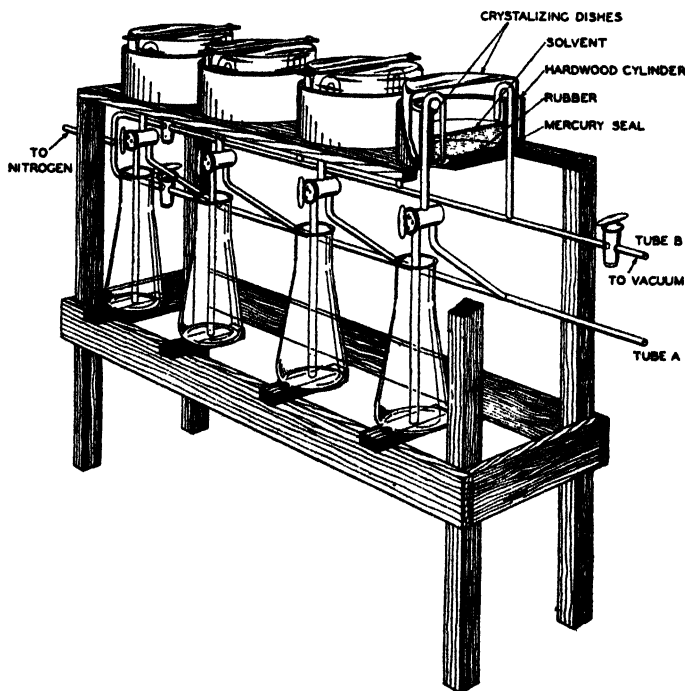


FIG. 1. Extraction apparatus

oxides which catalyze oxidation and it can be worked with more conveniently. The thickness of the sample before treatment was 30 to 35 mils. In the case of thick crepes and smoked sheets the samples were cut into thin ribbons.

The extraction was carried out in the apparatus shown in figure 1, employing 250 cc. of fresh solvent after each period of extraction. The samples were placed in a rust-free iron basket, which fitted into the extraction chamber. At the end of each extraction period the solvent was siphoned off and evaporated to final dryness in a vacuum at 70°C.; the amount of extract was weighed. The samples were not previously extracted with

acetone before treatment, since this is likely to result in oxidation of the hydrocarbon. The amount of soluble matter "resin," extracted overnight at room temperature by a mixture of 2 parts of petroleum ether and 3 parts of acetone, amounted to approximately 2.5 per cent for crepe and sheet and for dried latex film. The samples of latex films were dried on glass over phosphorus pentoxide in nitrogen at room temperature. In the extraction process the oxygen was displaced from above the samples by nitrogen. Every precaution was observed to avoid exposure of the latex and rubber samples to light and atmospheric oxidation.

TABLE 1

*Extraction of sol from various types of unmilled crude rubber**

RUBBER	PER CENT EXTRACTED AFTER						
	0.5 hr.	2.5 hr.	4 hr.	7 hr.	24 hr.	48 hr.	72 hr.
R.C.M.A. crepe (a)†	6.8	16.2	19.5	22.1	28.0	32.2	35.1
R.C.M.A. crepe (b)†	5.0	13.2	16.4	19.0	24.0	27.2	29.2
R.C.M.A. crepe (c)†	4.7	13.0	16.3	18.9	24.1	27.5	29.6
Water-white crepe	5.9	23.7	35.0	42.6	51.9	55.5	57.3
Yellow crepe	5.7	23.6	34.3	41.0	50.5	54.6	56.5
Purified crepe	17.2	47.8	57.4	62.2	66.6	68.5	69.2
No. 1 smoked sheet	5.9	13.8	18.8	24.1	35.4	44.5	49.0
No. 1A smoked sheet†	2.5	5.4	7.1	9.1	16.9	24.2	29.5
No. 1A smoked sheet§	1.0	2.5	3.0	3.6	6.8	10.2	13.2
Bolivian fine para	2.0	3.4	4.4	5.6	10.6	16.2	20.6

* The data are given as the total accumulated extract in per cent of the original sample at the end of each period.

† These samples were from the same bale. b and c were adjacent samples cut from the same sheet; a was cut from a different sheet.

‡ 33.2 per cent extract after 96 hr.

§ Uncut specimen 110 mils thick.

RESULTS

Sol extract in crude rubber

In order to standardize the method the first experiments were carried out on crude, unmilled rubber. These results are shown in table 1, and some of the data are plotted in figure 2.

The choice of a 72-hr. extraction period is of course somewhat arbitrary. After 72 hr. the rate of extraction of finely cut samples or very thin sheets becomes very slow. If much longer periods are employed, extreme care to guard against oxidation must be taken to be certain that the added sol is not the result of oxidation. Furthermore, a portion of what we are now considering as gel may have a definite, although a low, solubility in petroleum ether.

It is seen that, in the case of crepe specimens cut from the same sheet, the extraction procedure is capable of a satisfactory degree of reproducibility of results. The effect of varying the thickness of one of the smoked sheets is to slow up the extraction considerably, and it results in a large decrease in the total extract after 72 hr. extraction. The extraction is not complete after 72 hr.; however, this period of time is considered sufficient to extract all but the difficultly soluble hydrocarbon. Different lots of crepe and smoked sheets were found to vary nearly 100 per cent in their content of sol rubber. The lowest value was found in the case of the Bolivian fine ball rubber. It appears that a 72-hr. extraction in accordance with the above procedure is an excellent method for determining the ratio of sol and gel in crude rubber. It is preferable to operate at a constant

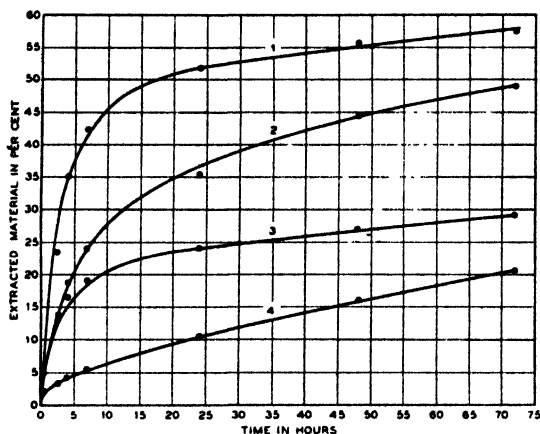


FIG. 2. Sol rubber content in crude rubber. Curve 1, water-white crepe; curve 2, European selected smoked sheet; curve 3, R.C.M.A. crepe; curve 4, Bolivian fine para ball.

temperature and to cut the samples very fine in order to obtain the most accurate results.

Sol rubber in dried latex films

Experiments were conducted to determine the amount of sol rubber in dried rubber films from fresh shipments of ammonia-preserved latex and from the same latex exposed to oxidizing influences after receipt.

The results presented in table 2 and plotted in figure 3 show that dried films of rubber from fresh commercial ammoniated normal latex contain only from 5.5 to 10 per cent extract after extraction for 72 hr. with petroleum ether. Upon exposure to air or light or when creped on rolls the content of sol rubber increases in proportion to the severity of the oxidizing treatment. After correcting for the 2.5 per cent acetone extract, the

amount of sol rubber hydrocarbon from the carefully protected latex rubber ranges from 3 to 7 per cent. In other words, sol rubber appears to

TABLE 2
Petroleum ether extraction of dried rubber films from latex

RUBBER	PER CENT EXTRACTED AFTER						
	0.5 hr.	2.5 hr.	4 hr.	7 hr.	24 hr.	48 hr.	72 hr.
Latex A, fresh shipment*	2.0	3.1	3.8	4.5	6.4	8.3	10.0
Latex A after moderate exposure to air†	1.8	3.1	4.2	5.0	8.3	12.5	15.9
Latex B, fresh shipment*	1.9	2.7	3.0	3.3	4.4	5.4	6.4
Latex B, fresh shipment†	1.7	2.6	3.4	4.0	5.6	7.2	8.5
Latex B after moderate exposure to air†	2.3	3.7	4.4	5.3	9.1	12.5	15.6
Latex B ₁	1.7	2.5	2.8	3.0	4.3	4.9	5.5
Latex B ₁ §	0.2	0.5	0.7	0.8	1.7	2.4	3.0
Latex B film heated 2 hr. at 80°C. in air	1.8	3.1	3.7	4.4	6.2	7.7	8.7
Latex B film exposed to sunlight for 6 hr.	1.7	2.5	3.0	3.4	5.1	7.5	9.6
Latex B film exposed 18 hr. under G.E. sun lamp	2.2	4.8	5.8	6.9	11.1	15.9	20.6
Latex B film creped through rolls¶	11.6	25.1	32.0	34.8	39.3	43.3	47.8

* The sample was taken on receipt. The drying and extraction were carried out in the dark and under an atmosphere of nitrogen.

† After keeping the latex for a few weeks and intermittently exposing it to the air.

‡ The sample was dried in the air and in the dark.

§ After deducting the acetone-soluble portion.

¶ Dried latex film rubber creped twelve times through even speed callender rolls until it resembled plantation crepe.

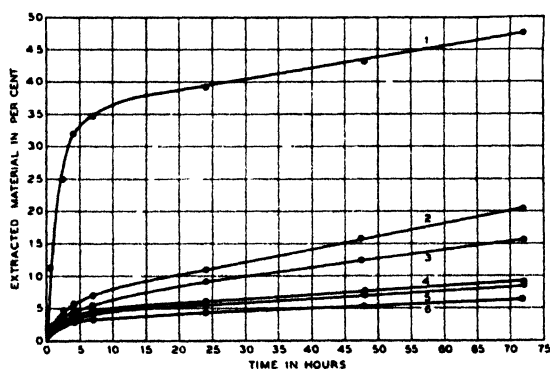


FIG. 3. Sol rubber in dried latex films. Curve 1, film creped twelve times through rolls; curve 2, film exposed 18 hr. under sun lamp; curve 3, film from latex exposed to air; curve 4, film heated 2 hr. in air at 80°C.; curve 5, film from fresh latex; curve 6, film from fresh latex prepared under oxygen-free conditions.

be a product resulting from oxidation of the gel rubber, which apparently comprises practically all of the rubber in the latex particles.

To study the effect of the thickness of the latex film, latex B₁ in a 31-mil film was compared with a finely cut 31-mil film and a 7-mil film. The results of extraction for 72 hr. were 2.9, 3.3, and 4.5 per cent, respectively, after correcting for the acetone extract.

It appears that the intermittent exposure of latex to air involved in the opening of a sealed can is sufficient to cause an increase in its sol rubber content. Extra handling and exposure to air may account for the higher sol content in latex A as compared with latex B. In view of this it would be of interest to determine sol in freshly tapped latex when quickly dried out of contact with light and oxygen. An experiment of this kind, however, would have to be carried out by those having laboratory facilities near the rubber-growing areas. A study should be made of the variation in sol content in latex from trees of varying age and environment under different tapping conditions as well as of the effect of adding ammonia and storing in drums.

Effect of different solvents on extraction of rubber

Since petroleum ether varies somewhat from lot to lot, the effect of using petroleum solvents having a variation in boiling range was determined. The results of this study are given in table 3 and show that small variations in the boiling range of petroleum ether do not affect the amount of extract from R. C. M. A. crepe, whereas the use of higher boiling ligroin increases the amount of extract considerably.

The results in table 3 show that a small increase in the extract from dried rubber latex films results from employing higher boiling petroleum fractions. These extracts resemble gel rubber in toughness, so that one must keep in mind that sol rubber varies from a soft state up to the tougher gel and that its solubility becomes lower as it approaches the gel state. No sharp line of demarcation of course exists.

The use of ethyl ether and the longer extraction period employed by Pummerer, Andriessen, and Gundel (6) explains the relatively higher content of sol rubber found by them. The high sol rubber content of purified rubber from latex found by Pummerer and coworkers is readily explained on the basis that oxidation of the gel component took place as a result of the purification treatment. The results on purified crepe in table 1 confirm this view. Furthermore, the purified rubber obtained by the Pummerer alkali purification process is amber in color, the color being the result of oxidation.

We have found that the sol rubber content determined by extraction with ethyl ether is higher than that found by employing petroleum ether. For example, dried latex films prepared from latex several weeks old had a 72-hr. petroleum ether extract of 15.9 per cent, whereas its ether extract

was 30.2 per cent when the same method of extraction was employed. It is well known that ether forms peroxides very readily, and it appears that the higher sol content found by employing ether is due to the oxidation of gel rubber to sol rubber by traces of peroxides almost always present in the ether or formed during the extraction process, owing to the fact that absolute exclusion of oxygen is not attainable.

In figure 6 there is shown the effect of changing from petroleum ether to ethyl ether (distilled over sodium and containing 0.001 per cent of peroxide) in the extraction of a dried latex film which had been exposed to air and contained a higher content of sol than usual. The increase in rubber

TABLE 3

Effect of different petroleum solvents on extraction of sol rubber from R.C.M.A. crepe and dried rubber latex film

SOLVENTS EMPLOYED	PER CENT EXTRACTED AFTER						
	0.5 hr.	2.5 hr.	4 hr.	7 hr.	24 hr.	48 hr.	72 hr.
Per cent extract of R.C.M.A. crepe							
Petroleum ether (b.p. 35-40°C.)	5.4	14.7	18.0	20.7	26.8	30.7	32.8
Petroleum ether (b.p. 35-58°C.)	5.4	14.9	18.1	20.6	26.5	30.5	32.8
Petroleum ether (b.p. 40-58°C.)	5.3	14.4	18.1	21.0	27.3	31.4	33.7
Ligroin (b.p. 80-90°C.)	5.3	20.0	27.0	31.7	38.5	43.0	45.7
Per cent extract of latex rubber film*							
Petroleum ether (b.p. 35-58°C.)	1.7	2.3	2.7	3.0	4.1	5.2	6.2
n-Hexane (b.p. 66-70°C.)†	1.8	3.0	3.4	3.8	5.2	7.3	9.2
Ligroin (b.p. 60-80°C.)	1.8	2.9	3.3	3.8	5.2	7.0	8.8
Ligroin (b.p. 80-90°C.)	1.8	3.1	3.6	4.2	6.0	7.8	9.7

* Latex B, fresh shipment.

† Skellysolve from Skelly Oil Co.

extract appears to be due not to an increased solubility of rubber in ethyl ether but to oxidation, since the ethyl ether-soluble fraction upon removal of the ether is freely soluble in petroleum ether. The effect of extracting with ethyl ether containing 1 per cent of benzoyl peroxide is also shown in figure 6.

Considerable work following that which is recorded in this paper has shown that normal hexane (Skellysolve), boiling between 66° and 70°C., is a more satisfactory solvent than petroleum ether for determining the sol rubber content. The sol content determined by the use of hexane is slightly higher than by the use of petroleum ether. The higher and narrower boiling range of hexane makes it easier and safer to handle than petroleum ether.

Treatment of latex with hydrogen peroxide

Hydrogen peroxide is sometimes used to bleach dark-colored latex. At the present time no test is employed to detect whether this or other chemical additions are injurious to the rubber in the latex. Table 4 gives the results of adding hydrogen peroxide in 0.3 and 3.0 per cent concentrations to the latex and allowing the latex to stand 48 hr. at room temperature after the hydrogen peroxide was added. It is seen that the addition of hydrogen peroxide results in a substantial increase in the sol rubber content.

TABLE 4

Effect of hydrogen peroxide on the sol rubber content of latex rubber

TIME OF EXTRACTION	PER CENT EXTRACT WITH PETROLEUM ETHER			
	Untreated latex*	Latex containing 0.3 per cent H ₂ O ₂		Latex containing 3.0 per cent H ₂ O ₂
<i>hours</i>				
0.5	1.7	1.6	1.9	2.0
2.5	2.3	3.0	3.2	3.7
4	2.7	3.7	3.8	4.5
7	3.0	4.4	4.5	5.5
24	4.1	6.9	6.7	9.8
48	5.2	10.8	11.0	16.4
72	6.2	14.6	14.9	24.0

* Latex B dried in nitrogen over phosphorus pentoxide.

TABLE 5

Effect of manganese and copper salts on the conversion of gel to sol rubber in latex

TIME OF EXTRACTION	UNTREATED LATEX	PER CENT EXTRACTED WITH PETROLEUM ETHER					
		0.1% Mn 48 hr. contact	0.1% Cu 48 hr. contact	0.1% Mn 11 days contact	0.1% Cu 11 days contact	0.3% Mn 24 hr. contact	0.3% Cu 24 hr. contact
<i>hours</i>							
0.5	1.7	2.3	2.2	4.7	2.5	8.6	3.1
2.5	2.3	3.9	4.0	15.3	5.3	29.1	8.6
4	2.7	4.7	5.0	23.6	7.6	45.2	12.9
7	3.0	5.6	6.4	32.6	10.7	54.4	20.0
24	4.1	8.4	11.4	46.8	20.2	61.4	37.5
48	5.2	11.1	17.0	51.7	27.1	63.5	44.5
72	6.2	13.5	22.7	53.6	32.0	65.1	48.4

Conversion of gel to sol rubber by catalytic oxidation

The effect of adding copper and manganese salts to normal latex was studied. Copper was added as copper sulfate in concentrations of 0.1 and 0.3 per cent copper based on the latex. Manganese in the same con-

centrations was added as the hydroxide. The latex was shaken from time to time over various periods, and the sol rubber content determined by the method as outlined. The results are given in table 5 and plotted in figures 4 and 5. The great activity of copper and manganese in catalyzing the conversion of gel to sol rubber by oxidation is evident. It is of interest

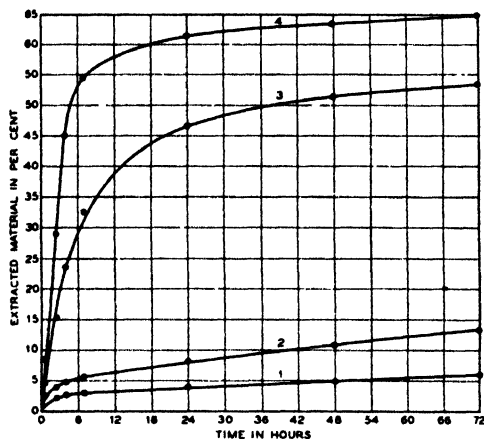


FIG. 4. Effect of manganese on gel-sol conversion in latex. Curve 1, control; curve 2, 0.1 per cent manganese after 48 hr.; curve 3, 0.1 per cent manganese after 11 days; curve 4, 0.3 per cent manganese after 24 hr.

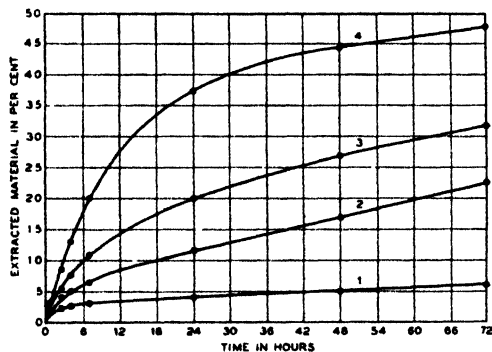


FIG. 5. Effect of copper on gel-sol conversion in latex. Curve 1, control; curve 2, 0.1 per cent copper after 48 hr.; curve 3, 0.1 per cent copper after 11 days; curve 4, 0.3 per cent copper after 24 hr.

to point out that even in the extreme cases of gel to sol conversion the latex film remained highly elastic. The sol rubber, however, in these cases was quickly converted to a viscous liquid when heated on the water bath and exposed to air, which resulted in further oxidation.

It is interesting to note that manganese in both concentrations is more

active than copper, except in the lower concentration for the shortest period.

Effect of milling

Kemp (4) has postulated that milling of rubber brings about a conversion of gel to sol rubber as a result of oxidation. The present work confirms this view.

To show the effect of milling, R.C.M.A. crepe was masticated for 5 min. on a cool laboratory mill. It was found that the total extract in 2.5 hr. increases from 13.0 per cent in the unmilled crepe to 45.4 per cent after milling. Further extraction resulted in the rubber breaking up into small flocs which were unavoidably siphoned off with the solvent, thereby making

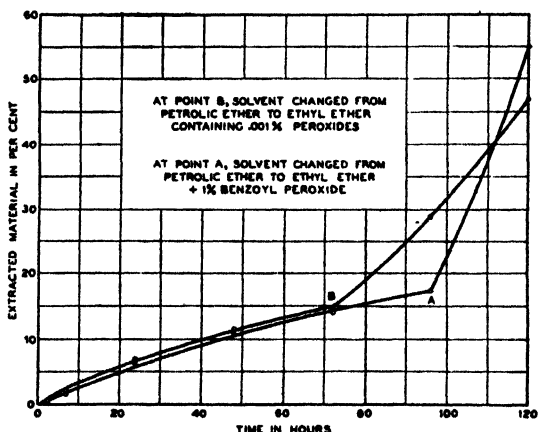


FIG. 6. Effect of ethyl ether on sol rubber extract

it impossible to determine the amount of extract after longer periods of extraction.

The results of milling are shown better in figures 7 and 8, taken after 1-g. cube-shaped samples of R.C.M.A. crepe from a 300-g. batch milled for various periods on a laboratory mill with cool rolls (opening 0.035 in.) were immersed in 100 cc. of petroleum ether for several days. The samples were re-photographed after they were lightly shaken by turning the tubes end-over-end a few times and the gel aggregates were allowed to settle. The hazy appearance of the solutions after shaking is due to the finely divided proteins and salts, which do not settle even after several weeks standing. This demonstration clearly shows that the gel is completely converted to sol after 10 to 20 min. of milling. Additional tests indicated that the conversion of gel to sol by milling was completed in less than 15 min. Continued milling probably results in further oxidation and break-down of the sol.

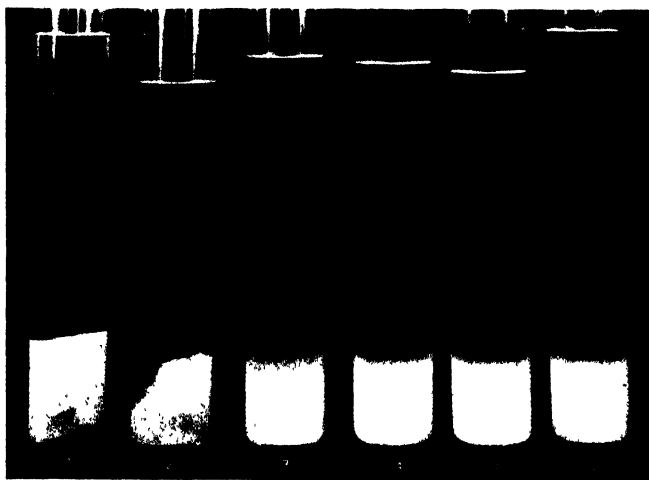


FIG. 7. Effect of milling on gel-sol conversion. 1, unmilled R.C.M.A. crepe; 2, milled 5 min.; 3, milled 10 min.; 4, milled 20 min.; 5, milled 30 min.; 6, milled 60 min.



FIG. 8. Effect of milling on gel-sol conversion. Conditions same as in figure 7, except that the contents were lightly shaken.

Effect of various solvents on swelling

Figures 9 and 10 show the swelling of 1-g. cubes of unmilled rubbers in 100 cc. of various solvents after standing 6 days in the dark. The proximate swelling and the sol rubber extract from 1-g. cubes of dried latex film rubber after the 6-day period in 100 cc. of different solvents are shown in table 6.

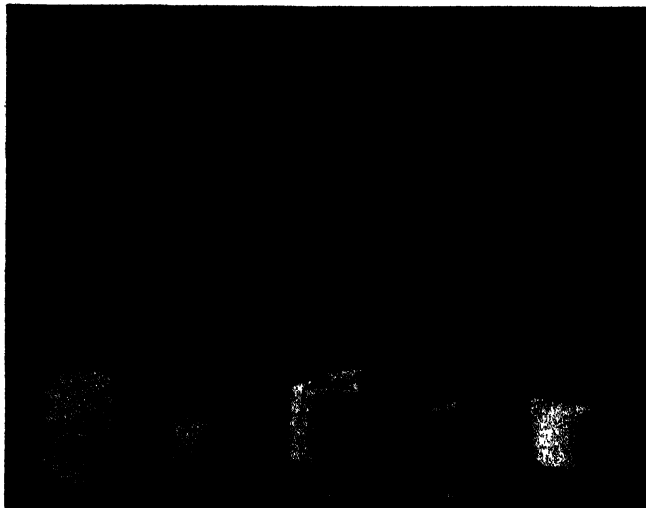


FIG. 9. Swelling of various types of unmilled raw rubber in petroleum ether. 1, purified crepe; 2, No. 1 smoked sheet, 75.5 Mooney shear viscosity; 3, No. 1 smoked sheet, 92 Mooney shear viscosity; 4, Bolivian fine para; 5, dried latex film

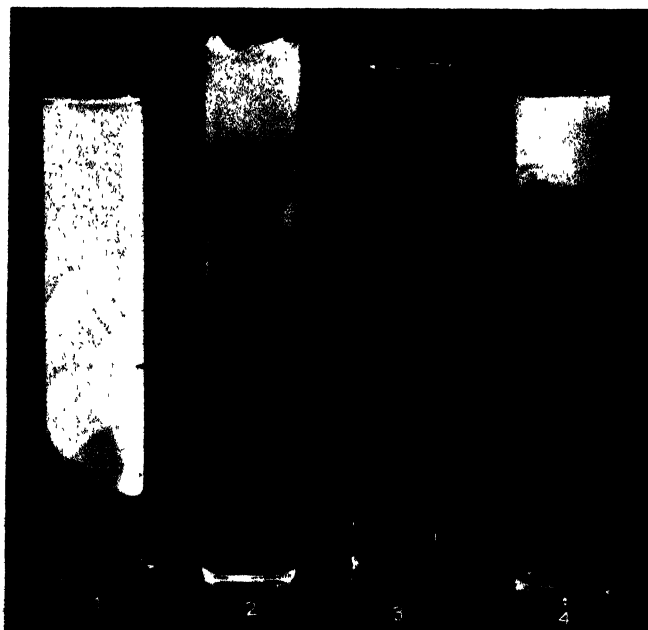


FIG. 10. Effect of various solvents on the swelling of dried latex film rubber. 1, carbon disulfide; 2, carbon tetrachloride; 3, benzene (line showing ton of swollen gel); 4, chloroform.

It is seen that the solubility of latex gel rubber is very low in various types of organic solvents. It is clear that the solubility and swelling of rubber depends on the nature of the rubber employed and the type of solvent used, and that one must therefore avoid generalizations in dealing with this subject. The literature on this subject is very confusing and sometimes misleading, since the nature of the rubber and the conditions of the experiments have not always been clearly defined. It is of interest

TABLE 6

*Proximate solubility and swelling of whole latex rubber in various solvents**

SOLVENT EMPLOYED	VOLUME OF CLEAR SOLUTION	VOLUME OF SWOLLEN GEL	SWELLING OF GEL	EXTRACT IN CLEAR SOLUTION†
	cc.	cc.	per cent	per cent
Petroleum ether	85	15	1500	3.4
Chloroform	82	18	1800	4.9
Benzene	76	24	2400	3.8
Carbon tetrachloride	60	40	4000	2.4
Carbon disulfide	22	78	7800	4.6

* 1 g. of rubber in 100 cc. of solvent in the dark for 6 days at room temperature.

† Shows the percentage of rubber soluble in solvents by diffusion.

TABLE 7

Swelling of various types of rubber in petroleum ether

SAMPLE	SWELLING	72-HR. SOL RUBBER EXTRACT
	per cent	per cent
Dried latex film	1500	5.5
Bolivian fine	1000	20.6
No. 1 smoked sheet*	2400	29.5
No. 1 smoked sheet†	1300	54.8
Purified crepe	2400‡	69.2

* Mooney shear viscosity 92.

† Mooney shear viscosity 75.5.

‡ Loose gel structure.

to note that, although the rubber in carbon disulfide is swollen to the point where the gel is like a thick cement, the clear carbon disulfide solution free from swollen gel contains about the same amount of total diffused extract as is present in the other solvents. These observations show that gel does not diffuse appreciably into a variety of organic solvents. This fact defines rubber gel.

The swelling of 1-g. cube-shaped samples of various types of rubber⁴

⁴ The samples of No. 1 smoked sheet and the Mooney shear viscosity values were given us by Dr. Gerke of the United States Rubber Company, whose courtesy is hereby gratefully acknowledged.

in petroleum ether after standing in 100 cc. of petroleum ether in the dark at room temperature for 6 days is given in table 7, along with their 72-hr. sol rubber extract. The swelling was determined by measuring the volume of the gel-free supernatant liquid and subtracting this from 100 to obtain the volume of the swollen gel, which is expressed as the increase in the volume of the original 1 cc. of rubber. It is apparent from these data that there is no relationship between the sol content and the extent of swelling.

The addition of 5 cc. of piperidine to the fully swollen gel in 100 cc. of petroleum ether and also in 100 cc. of benzene resulted in a considerable shrinking of the gel in both cases upon standing. This is not in agreement with the literature (8).

DISCUSSION OF RESULTS

This investigation indicates the value of the extraction method for studying the nature of the rubber in different lots of commercial latex to determine whether the conditions of preservation, storage, handling, or chemical treatment have affected the hydrocarbon.

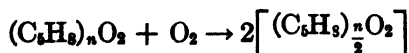
It also appears from the present work that rubber in the form of latex is very susceptible to oxidation upon exposure to air, which results in an increase in its sol rubber component. It further becomes apparent that the treatment of latex and coagulum on the rubber estates in the process of making crepe and smoked sheet results in sufficient oxidation of the gel rubber in the latex particle to convert a considerable portion of it to the soluble state. Variations existing in estate practice undoubtedly account for the wide range of sol content found in crude rubber.

Rubber which diffuses into petroleum ether is considered to be a molecular dispersion. The least soluble fraction contributes the greatest increase to viscosity and has the highest molecular weight. When unmilled crude rubber is placed in a hydrocarbon solvent and shaken in the absence of oxygen, the swollen gel is broken up and dispersed into small aggregates. A molecular weight determination of such a system by viscosity measurements may be somewhat indefinite, since only the gel portion of the rubber is not likely to be molecularly dispersed.

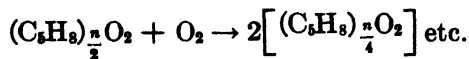
Since sol rubber results from oxidation of gel rubber, it is quite logical to expect it to contain a small quantity of combined oxygen. The double bond present in each C_6H_5 group in the rubber polymers offers the opportunity for oxygen addition as the moloxide or peroxide. Following this addition, rupture of the chain molecule can occur, leaving oxygen combined with both fragments. If the assumption is made that one molecule of oxygen splits a rubber molecule in two equal⁴ parts this can be expressed

⁴ It is assumed only for convenience that the chain is split in the middle. It could, of course, be split at any double bond.

by the following formula, assuming oxygen already combined at each end of the starting molecule.



and



The following oxygen contents calculated in the resulting products where n equals 10,000, 1000, and 100 are 0.005, 0.05, and 0.5 per cent, respectively. Midgley, Henne, Shepard, and Renoll (5) found by direct determination that sol rubber contains from 0.02 to 0.04 per cent of combined oxygen, which was increased to 0.44 per cent by milling. According to the above reaction mechanism a content of 0.04 per cent oxygen corresponds to a polymer having an average molecular weight of 80,000, which is of the same order as the average molecular weight found for sol rubber by the Staudinger viscosity method. Sol rubber oxidizes readily, and, if it reacted with 0.4 per cent additional oxygen upon milling, it is not at all unlikely that its average molecular weight would be reduced from 80,000 to about 8000.

It is recognized that oxygen may play the rôle of a polymerization or gelling catalyst as well as a depolymerization agent. Spence and Ferry (7) have recently found that sol rubber becomes insoluble when latex is treated with quinones. They attributed this to enhanced polymerization by linking the sol units with oxygen to form a gel.

Some investigators have considered sol and gel hydrocarbons as existing in some sort of a physical equilibrium wherein it is possible to convert gel to sol and back again to gel. The present work shows that gel is converted to sol by an oxidation process which ruptures the gel hydrocarbon, producing fragments of lower molecular weight with increased solubility in organic solvents. In this case the sol might be expected to contain more combined oxygen than the gel. On the other hand, it is possible to increase the solubility of the latex gel hydrocarbon in petroleum ether by the addition of a polar solvent such as alcohol or acetone; this is probably the colloidal effect known as peptization.

The mechanism of the reaction in which oxygen reacts with the gel hydrocarbon to form sol is not known. The small combined oxygen content of sol rubber and its increase on milling, as shown by Midgley and his coworkers (5), is evidence, however, that the reaction involves addition of oxygen to the double bond, followed by splitting of the gel molecules.

It cannot be decided on the basis of present evidence whether natural gel rubber is a single high polymer chain or fiber unit or whether there

exist cross-linking bonds between the long chains or fibers. Primary valence bonds existing between the polymeric chains would explain the swelling of gel rubber. The micellular theory involving associated bundles of fiber molecules held together by van der Waals forces has also been advanced to explain swelling. More research is needed in this field to clear up the picture.

It is now clear that rubber is subject to change from the time it flows from the wound in the tree. For this reason separate investigators are likely to reach different conclusions regarding the result of experiments on various lots of rubber latex or plantation grades, since the handling and processing of these materials involves many variables which are reflected in variations in the product. Aside from the variations in content of non-hydrocarbon constituents in latex and plantation rubber, the present work has shown that variations as regards the state of its hydrocarbon should be given greater consideration in the future.

The prevailing conception that latex globules are made up of a semi-fluid sol rubber center surrounded by a tough elastic shell may be questioned in view of the present work. The sol portion in crude rubber is the product from oxidation of the latex gel and is present in an amount which is dependent upon the extent of this oxidation. About 75 per cent of latex gel appears to be readily oxidized to sol, but the remainder requires a severe oxidative treatment such as milling to convert it to sol. This indicates that the hydrocarbon gel in latex may vary widely in molecular weight. The portion which is most difficult to break down would be expected to have the highest molecular weight.

SUMMARY

An apparatus and procedure to determine the amounts of sol and gel rubber in dried latex films and crude rubber have been described.

It is shown that while plantation smoked sheet and crepe contain large and varying quantities of rubber soluble in petroleum ether, dried rubber films from latex are practically free from sol rubber when oxidation has been avoided.

Latex increases in sol rubber content when subjected to various treatments permitting oxidation of the hydrocarbon. It appears from this work that the rubber in the form of latex is very susceptible to oxidation which, however, involves only minute quantities of combined oxygen.

When latex film rubber is subjected to creping it shows an increased content of sol rubber corresponding to that of crepe. A short milling of crepe was found to convert it completely into sol rubber. This confirms the gel-sol transformation mechanism of breakdown.

Gel rubber from dried latex films is swelled to a maximum of 1500 to 7800 per cent but is not dissolved when placed in benzene, chloroform,

carbon tetrachloride, or carbon disulfide and allowed to stand for several days. Gel rubber becomes soluble and therefore diffusible in these solvents as a result of oxidation.

It was found that dried latex film and various types of crude rubber swelled to a maximum of 1000 to 2400 per cent in petroleum ether and that this swelling was not proportional to the sol content.

This investigation strengthens the belief that sol rubber is an oxidation product of gel rubber. The formula for sol rubber is suggested as $(C_6H_8)_nO_2$ and a relationship between the molecular weight and the oxygen content is postulated on the basis that oxygen acts as a molecular splitting agent for both gel and sol.

REFERENCES

- (1) CASPARI, W. A.: *J. Soc. Chem. Ind.* **32**, 1041 (1913).
- (2) FEUCHTER, H.: *Kolloidchem. Beihefte* **20**, 434 (1925).
- (3) KEMP, A. R.: *Ind. Eng. Chem.* **19**, 551 (1927).
KEMP, A. R., AND MUELLER, G. S.: *Ind. Eng. Chem., Anal. Ed.* **6**, 52 (1934).
- (4) KEMP, A. R.: *Ind. Eng. Chem.* **30**, 154 (1938).
- (5) MIDGLEY, T., HENNE, A. L., SHEPARD, A. F., AND RENOLL, MARY W.: *J. Am. Chem. Soc.* **57**, 2318 (1935).
- (6) PUMMERER, R., ANDRIESEN, A., AND GUNDEL, W.: *Ber.* **61**, 1583 (1928); *Rubber Chem. Tech.* **2**, 367 (1929).
- (7) SPENCE, D., AND FERRY, J. D.: *J. Am. Chem. Soc.* **59**, 1648 (1937).
- (8) WHITBY, G. S.: *J. Phys. Chem.* **36**, 198 (1932).

A NEW DILATOMETER FOR DETERMINING BOUND WATER IN SOILS AND OTHER COLLOIDALLY DISPERSED MATERIALS¹

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The dilatometric method of determining bound water in soils, plant materials, and other colloiddally dispersed systems has been employed by a number of investigators, notably Anderson and Williams (1), Bouyoucos (2, 3), Foote and Saxton (4), Jones and Gortner (8), Hampton (6), McCool and Millar (10), and Sayre (12). In the field of soils the pioneer work has been done by Bouyoucos (2) with an apparatus of his own design and under a considerable variety of conditions.

In the course of an investigation to determine the changes in state of water in clays and soils when "puddled," i.e., mechanically worked within a critical range of moisture contents (11), it was found that concordant results could not be secured by the dilatometric method unless the conditions were rigorously controlled. The method is subject to all of the errors inherent in the measurement of the volume of liquids. Unless the temperature of the capillary is held constant, the ordinary variations in room temperature will introduce errors of considerable magnitude because of the relatively high coefficient of expansion of the reference liquid. Minute fluctuations in the temperature of the freezing bath introduce uncertainty into the measurements. The absolute quantity of reference liquid in the freezing tube determines in considerable measure the magnitude of this uncertainty. The technique should permit easy and complete evacuation of air from the sample and the setting of the column in the capillary to any desired initial height. To fulfill these conditions a new apparatus has been perfected, a description of which forms the basis of the present paper.

DESCRIPTION OF THE APPARATUS

A sketch of the dilatometer is shown in figure 1. Its principal features are a freezing tube, a special ground joint, and a three-way stopcock.

¹ Presented before the Division of Agricultural and Food Chemistry at the Ninety-sixth Meeting of the American Chemical Society, held in Milwaukee, Wisconsin, September 5-9, 1938.

The freezing tube, unlike the one of 60-cc. capacity in Bouyoucos' apparatus, was made elongated and slender to promote more rapid heat interchange and hence more rapid freezing. Its length below the ground joint is 11 cm. and its outside diameter 22 mm. Sample tubes are provided which are 10 cm. long and have an outside diameter of 18 mm. They will thus fit nicely into the freezing tube. These dimensions were chosen so that the tubes would conveniently hold about 25 g. of soil. The use of a

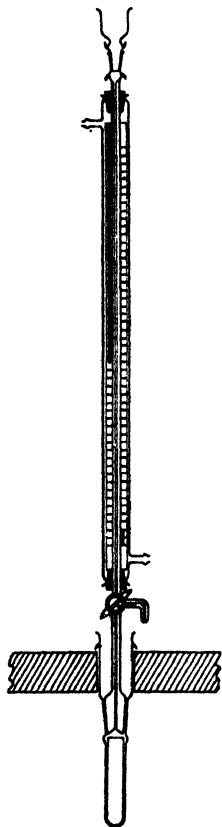


FIG. 1. Sketch of the dilatometer assembly

smaller tube to introduce the sample is very advantageous. It makes possible the preparation of a large number of samples in advance and a simple and rapid replacement of a measured sample with a fresh one. The annular space between the two tubes serves as a jacket which, though filled with the reference liquid, acts as a check against too rapid or premature freezing.

The ground joint was designed to have a taper corresponding to Corning No. 24/40 and hence to be interchangeable. The male part, though iden-

tical with No. 24/40 in taper, differs from it in having a 1-mm. bore. The latter has a cone-shaped enlargement at the bottom to permit easy escape of air bubbles during the evacuation.

The wide extension of the freezing tube above the ground joint is also a new feature. It is 9 cm. long above the joint and has an outside diameter of 4 cm. The obvious advantage of this elongation is to prevent leakage of the joint on contact with the freezing mixture. Unless so prevented, leakage is inevitable, since the stopcock grease, which must be toluene-proof, will of necessity be water-soluble. The grease used for this purpose was prepared by heating a mixture consisting of 60 per cent anhydrous glycerol, 20 per cent mannitol, and 20 per cent dextrin nearly to boiling with constant stirring until uniform. The viscosity of this grease can be easily regulated by varying the proportion of glycerol. On cooling it sets to a sticky mass which is entirely insoluble in toluene. It affords a vacuum-tight joint and has the additional advantage that, when placed in the freezing bath, the viscosity increases and makes the joint even more secure.

The extension gives the entire assembly somewhat greater sturdiness for handling. The hooks at the top make possible a firm attachment of the freezing tube by way of rubber bands stretched over the shoulder of the stopcock.

The three-way stopcock used here is Corning No. 2065, having a 1-mm. capillary T-bore, so arranged that it makes possible three operations: (1) evacuation of air from the sample; (2) filling with toluene from the bulb at the upper end of the capillary; and (3) removal of excess toluene and setting of the column to any desired height. The last operation is performed only after the freezing tube and contents have attained the temperature of the freezing bath. We have also used three-way stopcocks in which the three side arms were at an angle of 120° with each other and in which the plug had a curved bore connecting only two arms at one time. This type possesses some advantage over the T-bore type.

The tubes for measuring the expansion were carefully selected Pyrex capillary tubes of 1-mm. bore, so that a 50-cm. length had a volume of about 0.8 cc. The tubes themselves were not graduated. Instead, a special white porcelain scale was provided, with subdivisions similar to those of a Beckmann thermometer. This scale can be read to 0.2 mm., which corresponds to 0.0003 cc. in volume. Reference marks were etched on the capillary at the 0 and 50 cm. points. The capillary and scale,² together with a thermometer, were placed in an ordinary condenser jacket, so that this portion of the apparatus could be maintained at constant temperature by means of water circulating through it. When filled

² The excellent work of the manufacturers, Rascher and Betzold, Inc., of Chicago, Illinois, in the construction of the ground joints and scales is hereby acknowledged.

with water, the jacket itself acts as a lens, magnifying the scale and making it very easy to read. At the upper end of the capillary, attached by way of a ground joint, is a thistle tube through which the reference liquid can be easily introduced.

Originally a freezing bath consisting of crushed ice and salt, similar to that of Bouyoucos, was used. It was distressingly difficult to maintain the temperature of such a bath constant. To overcome this difficulty, a bath was designed in which the low temperature was produced by means of a $\frac{1}{4}$ H. P. Lipman compression unit. The inside dimensions of this bath were 8 x 10 x 42 in. It was lined with copper, heavily insulated with 3-in. cork-board, covered with a Monel metal top similarly insulated, and filled with a calcium chloride brine. It was equipped with a thermoregulator, expansion valve and coils, and an efficient stirrer. The regulator was capable of maintaining the temperature to $\pm 0.1^\circ\text{C}$.

Except when the measurements were made over a series of jacket temperatures, the jackets were maintained at $30^\circ\text{C} \pm 0.1^\circ$, by means of water circulating through them from a thermostat. For this purpose a Sargent circulating pump capable of giving a rate of flow of 4 liters a minute was employed. The entire assembly, which included three of the dilatometers as above described, made it possible to have conditions under positive control at all times and to speed up the measurements considerably.

CALIBRATION OF THE APPARATUS

Two calibrations are necessary before the apparatus can be used for determinations of bound water: (1) determination of the capillary scale readings in terms of true volumes; (2) determination of the amount of expansion obtainable with known amounts of water.

The first of these calibrations was made by weighing mercury delivered from the capillary through the side arm of the stopcock. In order to conform to the conditions of subsequent determinations, the temperature of the jacket was held at $30^\circ\text{C} \pm 0.1^\circ$. Since toluene wets the glass, while mercury does not, a small amount of it was placed on top of the mercury column, and all readings were made with respect to the toluene meniscus.

When true volumes are plotted against scale readings, the points are found to lie sharply on a straight line throughout the entire volume range. The algebraic equations representing the lines were as follows:

$$\text{Dilatometer No. 1.: } y = 0.01581x$$

$$\text{Dilatometer No. 2.: } y = 0.01542x$$

$$\text{Dilatometer No. 3.: } y = 0.01553x$$

in which y = the true volumes, calculated from the weights of mercury delivered, and x = the scale readings of the levels in the capillary tubes. The close agreement between the proportionality constants in these equations indicates the degree of uniformity that may be expected in carefully selected capillary tubes of apparently the same bore. In all subsequent work, these equations were employed in converting scale readings to true volumes, which was more satisfactory than taking the values from the graph.

The second calibration consisted in placing weighed amounts of water in the freezing tube and measuring the expansion obtained by the technique to be described in the next section. As before, the temperature of the jacket was held to $30^{\circ}\text{C.} \pm 0.1^{\circ}$ and the freezing bath to -3°C. When

TABLE 1
Expansion of water on freezing.

TEMPERATURE	EXPANSION IN CC. PER GRAM OF H_2O	INVESTIGATOR	REFERENCE
$^{\circ}\text{C.}$	cc.		
0	0.09073	Bunsen	(3)
0	0.09325	Foote and Saxton	(4)
-1	0.1 (approx.)	Bouyoucos	(3)
	0.09074	I. C. T.	(7)
	0.09402	Jones and Gortner	(8)
-1	0.09880	Sayre	(12)
	0.09400	Sayre	
	0.09680	Sayre	
	0.10000	Sayre	
	0.09880	Sayre	
-3	0.09565	Buehrer and Rosenblum	

the volume expansions are plotted against weights of water taken, a straight line is again obtained within the range of moisture contents studied (from 1 to 7 g.). Incidentally, these measurements were made in the absence of sea sand or any other solid material. The equation for the line is found to be

$$y = 0.09565x$$

where y is the observed expansion and x the weight of water in grams.

It is of interest to compare the factor, 0.09565, with those obtained by other investigators, as shown in table 1. These data indicate that a considerable variation is possible in this "constant," depending upon the kind of apparatus used, the technique employed, the rate of freezing, and the amount of solid material present, if any. In these respects the determination is highly empirical, necessitating not only a precise statement of the

conditions under which the determination is made but also a very careful control of those conditions. The fact that the observed expansions for different weights of water lie so consistently on a straight line with different dilatometers would indicate that the technique here described is reproducible and that the conditions are adequately controlled. These results also emphasize the fact that it is hazardous to apply a factor obtained by one investigator to measurements made by another unless measurements are made under identical conditions.

EFFECT OF TEMPERATURE

Variations in the temperature of the freezing bath as well as of the liquid in the capillary may introduce errors of considerable magnitude, which may not always neutralize each other. It appears from the published work of investigators in this field that the error due especially to the latter was assumed to be negligible and no provisions were made to insure constancy of temperature. Bouyoucos (3) controls the temperature of the freezing bath by hand, so far as that is possible with an ice-salt mixture, and recommends that "As the temperature of the bath does not remain constant throughout without frequent stirring, an effort is made to stir the mixture almost continuously. An excellent plan is to put into the bath about six dilatometers, . . . and then by holding the stems together at the top, move them up and down in the cold mixture." Evidently Bouyoucos makes no provision to maintain the temperature of the capillary constant. Even with the technique of agitating the freezing mixture by moving the dilatometers constantly up and down, it is unlikely that constancy of temperature is attained. We have found it practically impossible to hold an ice-salt mixture constant, even where the system was very effectively insulated against heat leakage and mechanical stirring was employed. Unless the capillary is kept at constant temperature with a water jacket as above described, the variations in room temperature may cause errors that are far from negligible, as will be shown in the following experiments.

Two independent sets of experiments were made to test the effect of temperature variations. In the first, the jacket was held constant at $30^{\circ}\text{C.} \pm 0.1^{\circ}$, and the freezing bath temperature held successively at different temperatures, ranging from -8.5° to -1.5°C. When the results were plotted, the curve was strictly linear over this range, and from its slope we found a volume change of 0.0293 cc. per degree. This may introduce an error of too large a magnitude to neglect if there is likelihood of variation in the bath temperature of several tenths of a degree. The absolute value of the slope of this line is dependent principally upon the amount of toluene present in the tube.

The second experiment was carried out in a similar manner, except that

the bath was held constant at $-3^{\circ}\text{C}.$ and the jacket temperature varied over a range from 8.5° to $40^{\circ}\text{C}.$ Again the points were found to lie on a straight line, and the mean rate of change, as shown by the slope, was 0.001099 cc. per degree Centigrade, which agrees with the coefficient of expansion of toluene previously published (7). The average per cent deviation from this mean value was found to be 2.3 per cent.

The foregoing coefficient enables us to apply a correction for the unavoidable expansion of the toluene which is forced up into the capillary as a result of the freezing of the water. The final volume measured in the capillary is obviously the sum of the true expansion which would have been obtained had the entire system been at the freezing temperature and

TABLE 2

Correction of dilatometer data for expansion of toluene due to temperature change

WEIGHT OF WATER	INITIAL SCALE READING	INITIAL VOLUME	FINAL SCALE READING	FINAL VOLUME	UN- CORRECTED EXPANSION	CORRECTED FOR TEM- PERATURE CHANGE	TRUE VOLUME	VOLUME EXPAN- SION PER GRAM OF H_2O
<i>grams</i>		<i>cc.</i>		<i>cc.</i>	<i>cc.</i>		<i>cc.</i>	<i>cc.</i>
1.0720	24.86	0.3869	31.55	0.4905	0.1036	0.00374	0.0998	0.09310
1.0720	24.66	0.3827	31.44	0.4880	0.1053	0.00383	0.1014	0.09459
2.0012	7.11	0.1120	20.21	0.3141	0.2021	0.0073	0.1948	0.09734
2.9871	14.86	0.2307	34.16	0.5300	0.2993	0.0109	0.2884	0.09655
5.0137	5.98	0.0920	38.46	0.5970	0.5050	0.0183	0.4867	0.09707
6.0244	6.53	0.1010	45.55	0.7070	0.6060	0.0220	0.5840	0.09694
7.0815	1.33	0.0209	45.83	0.7113	0.6914	0.0251	0.6652	0.09394
Mean								0.09565
Average deviation from the mean								0.00151
Per cent deviation								1.6

the increase in volume of the reference liquid due to the rise in temperature from that of the freezing bath to that of the jacket. Since the temperature conditions at the beginning and end of the determination are identical, the correction to be applied represents merely the change in the final volume as measured at $30^{\circ}\text{C}.$ back to $-3^{\circ}\text{C}.$ It is calculated by the simple equation:

$$V \cdot B (t_2 - t_1) = \text{Expansion due to temperature change}$$

in which V is the observed volume increase in the capillary, B the cubical coefficient of expansion of the toluene over this temperature range, and $t_2 - t_1$ the temperature range involved in the experiment. This is obviously a subtractive correction. For illustration we have assembled a typical set of data in table 2.

The point of particular importance in table 2 is the fact that the un-

avoidable expansion of the toluene forced into the capillary is of appreciable magnitude, being 3.6 per cent of the total expansion. The error so introduced would be even greater when working at lower temperatures. It is therefore evident that this expansion cannot justifiably be neglected in experiments where precision is needed or desired. Such a correction has not to our knowledge been hitherto applied by investigators employing the dilatometric method.

FINAL PROCEDURE

In the light of the foregoing experiments, the following procedure has been developed. The soil sample with the desired amount of water is weighed into the sample tube and allowed to stand to attain uniform moisture distribution. Having previously regulated the freezing bath and jacket temperature to -3°C . and 30°C ., respectively, the sample tube is introduced into the freezing tube, to the latter of which a small amount of anhydrous toluene (to a depth of about 1 in.) had been added. The toluene layer acts as a cushion and prevents the breaking of the sample tube while being introduced into the freezing tube. Toluene is now added to just cover the sample, and the freezing tube is attached to the apparatus at the lubricated ground joint. Rubber bands are stretched from hook to hook over the shoulder of the stopcock. The thistle tube at the top is filled with toluene.

The apparatus is lowered into the freezing bath and allowed to come to temperature. It is then connected to a Cenco Hyvac pump at the side arm of the stopcock and evacuated several times to remove air, toluene being added from above between evacuations. The size of the bubbles coming off usually indicates when all of the air has been removed. The entire apparatus is then filled with toluene and allowed finally to come to temperature in the freezing bath, which may require between 15 and 30 min. The level of the toluene in the capillary is then lowered by drawing off through the side arm of the stopcock to a convenient point on the lower end of the scale, and observations are taken at convenient time intervals until the level remains constant. If the sample is not mechanically disturbed, it will supercool nicely without premature freezing.

The sample is then frozen by surrounding it with an ice-salt mixture at -10°C . A sudden rise in the toluene level indicates when freezing has begun, after which the apparatus is immediately returned to the -3°C . bath. Observations of the toluene level are recorded at convenient time intervals, until it again becomes constant and remains so for 10 or 15 min. The entire time required for the level to become constant is usually from 30 min. to 1 hr. This period of time will depend upon the size of sample used. Occasionally the toluene column rises to a maximum value for an instant, then drops slightly and settles to a value which remains

constant over quite an interval of time. This effect may be attributed in part to the heat of fusion of the ice given out during the freezing, which, by reason of slow dissipation of the heat through the glass container, causes a momentarily abnormal expansion. As the heat is dissipated into the surrounding bath, the column settles down to a constant level.

From the reading of the toluene column before and after freezing, the expansion is calculated by using the calibration equation appropriate to the dilatometer used. The true volume expansion is then calculated by applying the expansion correction. Finally, the amount of water frozen is calculated from the corrected volume expansion, using the proper equation. These operations may be combined into one equation, for any one dilatometer, as follows:

Dilatometer No. 1

$$\frac{0.01581(S_f - S_i)[1 - 0.001099(t_2 - t_1)]}{0.09565W} \times 100 = \text{per cent of water frozen}$$

In this equation S_f and S_i are the final and initial scale readings, respectively, t_2 and t_1 the temperatures of jacket and bath, respectively, and W the weight of water initially taken. The numerical constants were determined as described in an earlier section. This equation simplifies to

$$\frac{0.1593(S_f - S_i)}{W} \times 100 = \text{per cent of water frozen}$$

As stated before, owing to the empirical nature of the dilatometric method, the interpretation of any results obtained with it should be made only in the light of the conditions of the determination. For that reason it is difficult to compare the results of two investigators on the same material when obtained under different conditions.

TEST OF REPRODUCIBILITY

In order to ascertain how closely the results obtained by means of different dilatometers will agree under the ordinary conditions of measurement described above, a test of reproducibility was made, using in this instance a solid phase in the form of purified sea sand. In the previous calibrations water alone was used. Twenty grams of sea sand and 4 g. of distilled water were weighed into the sample tubes, and the expansion of three such samples determined in each of the dilatometers. The sea sand was employed in this experiment to ascertain the order of magnitude of the effect of a solid phase which did not appreciably hydrate with water. The results are assembled in table 3. This table brings out several points of interest relative to the method. The mean expansion per gram of

water as shown in the last column is 0.0920 ± 0.0008 . The average deviations from the mean are in each case of the same order of magnitude, namely, about 1 per cent. Part of these deviations in the final expansion may be due to unknown variations in the fineness of the sand and possibly to a slight lag in the equalization of the temperature of the freezing bath between the intervals of operation of the compressor. It may be possible to minimize these deviations by still further refinement of the regulation.

Another peculiarity of the result is the order of magnitude of the expansion, i. e., 0.0920 cc. per gram of water with sand present, as compared with 0.09565 cc. per gram of water in the absence of a solid phase. This difference is beyond the experimental error of measurement. It indicates that the solid phase, which does not measurably hydrate with water, pos-

TABLE 3
Test of reproducibility

DILATOMETER NO.	DETERMINATION NO.	WEIGHT OF WATER	TRUE EXPANSION	EXPANSION PER GRAM OF WATER	MEAN FOR EACH DILATOMETER
		<i>grams</i>	<i>cc.</i>	<i>cc.</i>	<i>cc.</i>
1	1	3.9951	0.3699	0.09259	0.0925 ± 0.0010
1	2	3.9876	0.3630	0.09104	
1	3	3.9859	0.3746	0.09398	
2	1	3.9514	0.3587	0.09078	0.0908 ± 0.0007
2	2	3.9886	0.3581	0.08978	
2	3	3.9928	0.3670	0.09191	
3	1	3.9686	0.3658	0.09217	0.0928 ± 0.0008
3	2	3.9850	0.3672	0.09214	
3	3	3.9887	0.3758	0.09422	
General average.....					0.0920 ± 0.0008

sibly exerts a capillary effect which prevents some of the water from freezing. A part of the water usually classed as "bound" may therefore be not only chemically combined but also held by purely physical forces. The results of investigations in this field carried out by the technique here presented will be set forth in a subsequent series of papers.

SUMMARY

1. A new dilatometer has been perfected which makes possible a precise control of experimental conditions.
2. The effect of changes in the temperature of the freezing bath and the capillary have been investigated, and a quantitative expression for the correction to be applied to the observed data has been presented.
3. It is shown that when conditions are so controlled and the proper corrections are applied to the measurements, the results obtained by any one observer are reproducible within 1 to 2 per cent.

REFERENCES

- (1) ANDERSON, D. B., AND WILLIAMS, C. F.: *Plant Physiol.* **7**, 175 (1932).
- (2) BOUYOUCOS, G. J.: *Michigan Agr. Expt. Sta. Tech. Bull.* **36** (1917).
- (3) BOUYOUCOS, G. J.: *Soil Sci.* **42**, 217 (1936).
- (4) FOOTE, H. W., AND SAXTON, B.: *J. Am. Chem. Soc.* **38**, 588 (1916); **39**, 1103 (1917).
- (5) GREATHOUSE, G. A., AND PARKER, M. W.: *Plant Physiol.* **11**, 209 (1936).
- (6) HAMPTON, H. C.: *Science [N.S.]* **63**, 49 (1926).
- (7) *International Critical Tables*, Vol. III, p. 27. McGraw-Hill Book Co., Inc., New York (1928).
- (8) JONES, I. D., AND GORTNER, R. A.: *J. Phys. Chem.* **36**, 387 (1932).
- (9) *Landolt-Börnstein Tabellen*, 4 Aufl., p. 346 (1912).
- (10) MCCOOL, M. M., AND MILLAR, C. E.: *Botan. Gaz.* **70**, 317 (1920).
- (11) McGEORGE, W. T.: *Arizona Agr. Expt. Sta. Tech. Bull.* No. 67 (June, 1937).
- (12) SAYRE, J. D.: *J. Agr. Research* **44**, 669 (1932).

NEW BOOKS

Physical Constants of Hydrocarbons. By GUSTAV EGLOFF. 9 x 6 in.; 403 pp. New York: Reinhold Publishing Corporation, 1939. Price: \$9.00.

The author has set an ambitious goal for himself in undertaking to assemble the physical constants of all hydrocarbons. As he himself remarks, this field has been developed at such a rapid pace in recent years that the older reference works have not only become entirely inadequate for our present-day needs but also do not summarize a large volume of information available in the more recent literature.

This first volume covers the paraffins, olefins, acetylenes, and other aliphatic hydrocarbons. Two other volumes which are to follow will contain the physical constants of all the remaining classes of pure hydrocarbons, and the fourth volume will bring out existing interrelationships in the form of an analysis designed to disclose possible errors in experimental values for individual compounds and to permit the prediction of the physical properties of hydrocarbons which are as yet unknown or not investigated.

The present series gives (1) melting points, (2) boiling points, (3) specific gravities, and (4) refractive indices. Additional studies are under way, aiming toward subsequent compilations of data on the following: critical pressures, temperatures, and volumes; viscosities, surface tensions, and specific heats; heats of formation, of vaporization, and of fusion; free energies, entropies, parachor values, and octane numbers.

The author has made use of all available sources of information and thinks that he has succeeded in incorporating all data available to November, 1938. However, those who will be using this book for reference purposes will appreciate how nearly impossible it is to incorporate everything in such a survey, and, rather than be overcritical in regard to any omissions that they may find, they should gladly cooperate with Dr. Egloff in his appeal for communications in regard to missing data.

The author has undoubtedly done the right thing in adopting the Geneva system of nomenclature. However, readers who have not been brought up on this system will have no difficulty in orienting themselves, for the corresponding structural formulas are given in all cases. That the Geneva system is not always so clear and simple as it was designed to be, is brought out by Dr. Patterson's interpretation of it, as quoted verbatim by the author. Thus, the illustration given to bring out the meaning of rule 6 is obviously a violation of the subsequent rule 7. In his interpretation of the Geneva system, Dr. Patterson doubts that the replacement of "ethylene" by "ethene" will ever become general and considers it unlikely that the time-honored "acetylene" will be replaced by "ethyne." Dr. Egloff has solved this difficulty by going halfway in that, for some unknown reason, he has rejected our old friend "ethylene" but has retained "acetylene."

The author's review of the methods employed in the critical evaluation of the data and in the calculation of the most probable values seems very convincing and should be satisfactory for most purposes. By such a systematic study and recalculation of available results, it has been possible for him to give us comparable values for the various hydrocarbons on which sufficient data are available. The data that are considered most reliable are shown in boldface print. In some instances, it has undoubtedly been difficult to select the most reliable data. Thus, in the case of

butadiene-1,3, the author had to choose between Kistiakowsky's boiling point of -4.51°C . at 757 mm., as determined in 1936, and that of -2.6°C . at 760 mm.; as determined by Grosse in 1937, and so he has preferred to omit the boldface.

There is a natural tendency to examine a volume of this kind with a rather critical mind, and the present reviewer is no exception in this respect. However, if the work has any shortcomings, these are not at all obvious. On the contrary, university workers and industrial people alike—who are in any way concerned with the properties of hydrocarbons—will find this compilation most useful as a reference work, and they should be thankful to the author for having made available to them the sources of information at his disposal.

Any errors that may have crept in during the assembling and transcription of data cannot be detected in a preliminary review. It remains for the users of this reference work to express an opinion on that point. In the meantime, the reviewer notes with satisfaction that Dr. Egloff has at least done away with certain frequently quoted erroneous data, such as some of the values which have appeared for the melting point of butadiene and for the boiling point of pentene-1.

PER K. FROLICH.

Proceedings of the Sixth Summer Conference on Spectroscopy and its Application. 6 x 9 in.; 5 figures; vii + 172 pp. New York: John Wiley and Sons, Inc., 1938. Price: \$3.00.

The Technology Press has published in the present volume in somewhat condensed form the thirty-one papers presented at the Sixth Summer Conference on Spectroscopy held at the Massachusetts Institute of Technology in July, 1938. The applications to varied fields are well represented, as well as the theoretical aspects. The discussions are not reproduced.

S. C. LIND.

The Principles of Electrochemistry. By DUNCAN A. MACINNES. 478 pp.; 150 illustrations. New York: Reinhold Publishing Corporation, 1939. Price: \$6.00.

In the preface the author emphasizes that the "subject of electrochemistry has become so extended" that it was necessary to "severely limit the range of topics considered."

Accordingly, the author has confined himself to the principles of electrochemistry of aqueous solutions,—in particular, very dilute solutions. His treatment of these has been most thorough and is based on many years of careful application to the subject. In the twenty-four chapters the following topics, among others, are considered: the laws of Faraday, electrolytic conductance, electrolytic transference, the principles of thermodynamics, the Debye-Hückel theory, concentration cells, standard electrode potentials, determination of pH, electrometric titrations, the dielectric constants of liquids, electrokinetic phenomena, and passivity and over-voltage.

Most of the experimental data referred to in the book are of relatively recent origin, having been obtained during the last ten or fifteen years.

To all interested in the physical chemistry of solutions this book is highly recommended.

COLIN G. FINK.

THE OXIDATION OF SOLUTIONS OF FERROUS SALTS

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Received January 8, 1938

The author has made previously some experiments on the oxidation of ferrous sulfate solutions (1); the present work is an extension of these experiments. Solutions of various ferrous salts were exposed to the air at room temperatures and higher, and the oxidation that occurred was found by titration with 0.1 normal oxidizing agent before and after the exposure. Generally the ferrous salt solutions (5 cc.) were placed in test tubes 2.5 cm. in diameter, and other reagents were added as desired. The quantities of all reagents are expressed in gram-moles per liter. It was necessary to run comparatively small batches at a time, but these may be readily correlated.

Selected results with 0.1 molar solutions of ferrous salts are given in tables 1 and 2; table 3 shows results obtained with other than 0.1 molar solutions. In each series of experiments the "blank", i.e., the cubic centimeters of $N/10$ oxidizing agent equivalent to the original solution, is given after the heading of the series in parentheses: e.g., in table 1(a) the 5 cc. of original ferrous sulfate solution was equivalent to 3.38 cc. of $N/10$ permanganate solution (this is an exceptionally low value).

Duplicate experiments are not quoted, and many confirmatory tests are omitted. In each series the temperature varied over a few degrees, the average being quoted; but the experiments of each series were, of course, performed under the same conditions.

EXPERIMENTS WITH AQUEOUS SOLUTIONS OF FERROUS SALTS

The ferrous sulfate solution of table 1(a) was part of a large stock which was originally 0.1 molar in ferrous sulfate and 0.05 molal in sulfuric acid. Thus the presence of considerable ferric salt does not affect the oxidation. The solutions of table 2(a) were made from an exact weight of ferrous sulfate crystals in each test tube. Here the solution without any added acid gave a precipitate within 3 hr.; after 5 days it contained an appreciable brown precipitate, but the liquid was colorless; the other solutions containing acid were clear and colorless throughout.

Solutions of series 1(b), 1(c), 2(c), and 2(d) were made from ferrous sulfate crystals and were filtered immediately from a slight precipitate;

TABLE 1

Results obtained with N/10 solutions of ferrous salts at room temperature

The extent of oxidation is expressed in terms of cubic centimeters of N/10 oxidizing agent; the concentrations of the reagents in gram-moles per liter. The oxidation equivalent of the ferrous salt taken (and thus also of complete oxidation) is given in parentheses after the heading of each series

(a) FeSO ₄ solution; 9 days at 18°C. (3.38 cc.)			(e) FeCl ₃ solution; 9 days at 14°C. (4.99 cc.)		
H ₂ SO ₄	REAGENT	OXIDATION	HCl	REAGENT	OXIDATION
0.05		0.06	0.1		0.07
0.30		0.03*	5.5		2.44*
0.05	0.17 H ₂ PO ₄	0.39	0.05	2.5 (NH ₄) ₂ SO ₄	0.09*
0.05	0.5 H ₂ PO ₄	1.27*	0.05	0.17 H ₂ BO ₃	0.00*
0.05	1.5 H ₂ PO ₄	2.46	0.1	0.17 HNO ₃	0.10
0.05	2.7 H ₂ PO ₄	2.97	0.05	0.5 HNO ₃	0.10*
0.05	8.0 H ₂ PO ₄	2.48*			
(b) FeSO ₄ solution; 14 days at 8°C. (5.41 cc.)			(f) Fe(NO ₃) ₃ solution; 14 days at 12°C. (4.85 cc.)		
H ₂ SO ₄		OXIDATION	HNO ₃	REAGENT	OXIDATION
0.00005		0.11†	0.01		0.00
0.005		0.06	0.17		0.07
0.01		0.12	0.2		0.00
0.02		0.12	0.3		1.11
	plus CaCO ₃	0.68†	0.4		4.85
			0.01	0.1 H ₂ SO ₄	0.03
			0.01	0.8 H ₂ SO ₄	0.05
			0.01	0.17 HCl	0.06
			0.01	0.01 NaNO ₂	1.05
(c) FeSO ₄ solution; 7 days at 7°C. (5.34 cc.)			(g) Fe(ClO ₄) ₃ solution; 14 days at 12°C. (4.84 cc.)		
H ₂ SO ₄		OXIDATION	HClO ₄	REAGENT	OXIDATION
0.00015		0.04	0.02		0.04
0.00015 plus 0.0001 NaOH		0.07†	0.02	0.2 HNO ₃	0.07
0.00015 plus 0.0003 NaOH		0.10†	0.02	0.1 H ₂ SO ₄	0.13
0.00015 plus 0.0006 NaOH		0.11†			
0.00015 plus 0.01 H ₂ PO ₄		0.20†			
(d) FeCl ₃ solution; 7 days at 13°C. (5.05 cc.)			(h) Fe(H ₂ PO ₄) ₃ solution; 16 days at 11°C. (4.10 cc.)		
HCl	REAGENT	OXIDATION	H ₂ PO ₄		OXIDATION
0.1		0.07	0.16		2.69†
0.7		0.10*	0.4		3.08
1.9		0.33	2.9		3.87
0.1	0.8 H ₂ SO ₄	0.14			
0.05	0.5 H ₂ PO ₄	2.09*			
0.1	2.7 H ₂ PO ₄	3.43			
0.1	0.3 H ₂ PO ₄	2.01			
0.1	0.5 H ₂ PO ₃	2.77			
0.05	1.0 NH ₄ Cl	0.04*			
0.05	2.5 NaCl	0.14*			
0.1	0.02 NaNO ₂	2.27			
(i) Fe(C ₂ H ₃ O ₂) ₃ solution; 1 day at 9°C. (5.40 cc.)			HC ₂ H ₃ O ₂	REAGENT	OXIDATION
			(0)		0.48†
			3		0.13†
			0.01	0.045 H ₂ SO ₄	0.17†
			0.01	0.095 H ₂ SO ₄	0.00
			(0)	0.15 NaC ₂ H ₃ O ₂	0.86†
			(0)	plus CaCO ₃	0.58†

TABLE 1—Continued

(j) $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution; 3 days at 8°C. (5.16 cc.)			(l) $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution; 1 and 2 days at 8°C. (4.29 cc.)			
$\text{HC}_2\text{H}_3\text{O}_2$	REAGENT	OXIDATION	REAGENT	OXIDATION (1 DAY)	OXIDATION (2 DAYS)	
(0)		1.26†				
(0)	plus CaCO_3	1.37†		0.38	0.73	
0.01	0.005 H_2SO_4	1.25†	0.1 H_2SO_4	0.01		
0.01	0.015 H_2SO_4	0.95†	0.0075 $\text{NaC}_2\text{H}_3\text{O}_2$	0.39		
0.01	0.040 H_2SO_4	0.48†	0.015 $\text{NaC}_2\text{H}_3\text{O}_2$	0.43		
0.01	0.045 H_2SO_4	0.39†	0.030 $\text{NaC}_2\text{H}_3\text{O}_2$	0.43	0.77†	
0.01	0.095 H_2SO_4	0.05	0.12 $\text{NaC}_2\text{H}_3\text{O}_2$	0.55	0.94	
(k) $(\text{CH}_3\text{COO})_2\text{Fe}$ solution; 1 day at 12°C. (4.69 cc.)			0.21 $\text{NaC}_2\text{H}_3\text{O}_2$		0.97*	
REAGENT		OXIDATION	0.37 $\text{NaC}_2\text{H}_3\text{O}_2$		0.90*	
		0.69†	0.0089 $\text{HC}_2\text{H}_3\text{O}_2$	0.38		
0.1 H_2SO_4		0.04	0.027 $\text{HC}_2\text{H}_3\text{O}_2$	0.25	0.62	
0.04 H_3PO_4		0.67†	0.054 $\text{HC}_2\text{H}_3\text{O}_2$	0.26	0.53	
0.1 H_3PO_4		0.40†	0.18 $\text{HC}_2\text{H}_3\text{O}_2$	0.21	0.37	
0.32 H_3PO_4		0.27	0.44 $\text{HC}_2\text{H}_3\text{O}_2$		0.12†	
0.07 (?) $(\text{CH}_3\text{COOH})_2$		0.44†				
0.1 (?) $(\text{CH}_3\text{COOH})_2$		0.24†				
0.05 $(\text{CH}_3\text{COONa})_2$		0.72†				
0.11 $(\text{CH}_3\text{COONa})_2$		0.77†				
0.12 $\text{NaC}_2\text{H}_3\text{O}_2$		0.86†				
(m) FeSO_4 and $\text{Fe}(\text{SO}_4)_2$ solution; 2 and 4 days at 18°C. (5.66 cc.)						
REAGENTS			OXIDATION (REDUCTION IS GIVEN IN PARENTHESES WITH MINUS SIGNS)			
H_2SO_4	$\text{H}_2\text{C}_2\text{O}_4$	Citric acid	2 days in the light	2 days in the laboratory	4 days in the laboratory	4 days in the dark
0.05	0	0	0.13		0.01	0.03
0.10	0	0	0.01			0.03
0.05	0	0.001	(-0.25)			0.08
0.05	0	0.005	(-1.08)		(-0.16)	0.00
0.05	0	0.01		(-0.10)		0.07
0.05	0.0004	0	(-0.04)			(-0.01)
0.05	0.002	0	(-0.34)		(-0.14)	(-0.10)
0.05	0.004	0	(-0.70)	(-0.14)		0.03
0.50	0	0.005	(-0.06)		0.10	
0.05	0.8 H_3PO_4	0.005			1.19	

TABLE 1—*Concluded*(n) FeSO_4 solution; 15 days at 17°C . in the dark (5.21 cc.)

REAGENTS		OXIDATION	REAGENTS		OXIDATION
Sulfuric acid	Citric acid		Sulfuric acid	Oxalic acid	
0.05	0	0.21	0.05	0	0.21
0.05	0.004	0.23	0.05	0.004	0.27
0.05	0.014	0.29‡	0.05	0.016	0.29
0.05	0.025	0.24	0.05	0.032	0.41
0.05	0.1	0.34	0.05	0.1	0.38†
0.05	0.2	0.43	0.05	0.2	0.29†
0.05	0.5	0.69	0.05	0.5	0.42†
0.55	0.0	0.16	0.55	0.0	0.16
0.55	0.025	0.17	0.55	0.032	0.21
0.55	0.1	0.23	0.55	0.1	0.84‡
0.05	0.1 H_3PO_4	4.13			

* In these experiments the concentration of the ferrous salt was lowered, generally halved, by addition of the reagent solution.

† Precipitates were formed here soon after the start of the experiment.

‡ A trace of precipitate was formed before the end of the experiment.

§ This value is certainly high.

more precipitate formed in these solutions when they were kept at room temperature. In the first experiment of table 1(b) the pH fell from 3.9 to 3.0, and in the first experiment of table 1(c) the pH fell from 3.5 to 3.3. The first experiments of table 1(k) and table 1(l) had pH values of 5.0 and 2.5, respectively.

In series 2(c) after 6 days the solution with no added acid was yellow and contained considerable yellow-brown precipitate; the next solutions with increasing acid were decreasingly straw-colored; and the last solution was colorless. The first solution in 2(c) changed during the 6 days from pH 3.9 to 2.6, i.e., from 0.00005 M to 0.001 M sulfuric acid; this increase in acidity proceeded at a diminishing rate, i.e., the acidity developed most rapidly at the start. The first solutions in 2(d) and 2(i) had pH values of 3.5 and 2.1, respectively.

In series 2(d) the solutions with less than 0.005 molar acid gave precipitates; here the more alkali was used to reduce the acid concentration, the greater was the amount of precipitate, but the oxidation was not increased proportionately. The alkali probably precipitated a proportional amount of basic ferric salt early in the experiment, and thus the total oxidation would be the same as that occurring in the original "neutral" solution. When the ferrous salt solutions were in contact with solids like calcite, zinc oxide, and magnesia, which would continuously reduce the acid concentration, the solutions were rapidly oxidized.

TABLE 2
Results obtained with N/10 solutions of ferrous salts

(a) FeSO ₄ solution; 5 days at 28°C. (5.2 cc.)			(f) FeCl ₂ solution; 4 days at 26°C. (4.92 cc.)		
H ₂ SO ₄		OXIDATION	HCl		OXIDATION
(0)		0.45†	0.1		0.11
0.05		0.30	1.9		0.85
0.1		0.31	3.2		1.99
0.2		0.29	4.2		3.22*
			5.0		4.06*
(b) FeSO ₄ solution; 8 days at 27°C. (3.13 cc.)			(g) FeCl ₂ solution; 7 days at 26°C. (4.88 cc.)		
H ₂ SO ₄		OXIDATION	HCl	REAGENT	OXIDATION
0.05		0.28	0.1		0.10
1.7		0.13	1.1		0.30
6.0		0.10	0.1	0.33 H ₃ BO ₃	0.14
			0.1	0.05 Na ₂ B ₄ O ₇	0.20†
			0.1	0.35 HC ₂ H ₃ O ₂	0.07
			0.1	1.7 HC ₂ H ₃ O ₂	0.10
			0.1	0.15 NaC ₂ H ₃ O ₂	1.08†
			(0.1)	plus CaCO ₃	0.90†
			(0.1)	plus ZnO	1.42†
			(0.1)	plus MgO	3.60†
			(0.1)	plus BaCO ₃	1.31†
(c) FeSO ₄ solution; 6 days at 28°C. (5.41 cc.)			(h) FeCl ₂ solution; 8 days at 27°C. (4.91 cc.)		
H ₂ SO ₄		OXIDATION	HCl	REAGENT	OXIDATION
0.00005		0.59†	0.1		0.23
0.005		0.52	1.9		1.03
0.01		0.54	0.1	0.06 H ₃ BO ₃	0.16
0.02		0.54	0.1	1.8 MgCl ₂	0.53*
0.05		0.41	0.1	2.3 NaCl	0.16*
			0.1	5.6 NH ₄ Cl	0.56
			0.1	Platinum black	4.00
(d) FeSO ₄ solution; 3 days at 28°C. (5.34 cc.)			(i) Fe(NO ₃) ₃ solution; 3 days at 26°C. (5.17 cc.)		
H ₂ SO ₄	REAGENT	OXIDATION		REAGENT	OXIDATION
0.00015		0.37†			0.12
0.005		0.37		0.02 H ₃ PO ₄	0.27†
0.00015	0.01 HCl	0.30		0.04 H ₃ PO ₄	0.36†
0.00015	0.01 H ₃ PO ₄	0.56†		0.1 H ₃ PO ₄	0.87†
0.00015	0.014 H ₃ BO ₃	0.50†		0.2 H ₃ PO ₄	1.19
0.00015	0.0001 NaOH	0.35†		plus CaCO ₃	0.6†
0.00015	0.0003 NaOH	0.43†		0.03 NaC ₂ H ₃ O ₂	0.12
0.00015	0.0006 NaOH	0.43†		0.12 NaC ₂ H ₃ O ₂	2.1†
0.00015	0.001 NaOH	0.43†			
(e) FeCl ₂ solution; 4 days at 25°C. (4.92 cc.)					
HCl	REAGENT	OXIDATION			
0.1		0.11			
0.32		0.07			
1.9		0.37			
0.1	2.7 H ₃ PO ₄	4.00			
0.1	0.8 H ₂ SO ₄	0.19			

* In these experiments the concentration of the ferrous salt was lowered, generally halved, by addition of the reagent solution.

† In these cases a precipitate formed during the experiment.

TABLE 3

Results obtained with ferrous salt solutions of various concentrations

(a) Various ferrous salt solutions; 14 days at 12°C.

SOLUTION	ADDED REAGENT	OXIDATION
$M/10 \text{ Fe}(\text{NO}_3)_2$	None	0.00
	0.2 $M \text{ HNO}_3$	0.03
$M/10 \text{ Fe}(\text{ClO}_4)_2$	None	0.04
	0.2 $M \text{ HNO}_3$	0.07
$M/4 \text{ Fe}(\text{NO}_3)_2$	None	0.22
	0.2 $M \text{ HNO}_3$	0.39
$M/4 \text{ Fe}(\text{ClO}_4)_2$	None	0.14
	0.2 $M \text{ HNO}_3$	0.21
$M/2 \text{ Fe}(\text{NO}_3)_2$	None	0.88
	0.2 $M \text{ HNO}_3$	1.27

(b) Ferrous phosphate solutions; 16 days at 11°C.

SOLUTIONS	ADDED REAGENT	OXIDATION
$M/12 \text{ Fe}(\text{H}_2\text{PO}_4)_2$	0.16 $M \text{ H}_2\text{PO}_4$	2.69†
	3.0 $M \text{ H}_2\text{PO}_4$	3.87
$M/5 \text{ Fe}(\text{H}_2\text{PO}_4)_2$	0.4 $M \text{ H}_2\text{PO}_4$	7.75
	3.0 $M \text{ H}_2\text{PO}_4$	6.90
$M/2 \text{ Fe}(\text{H}_2\text{PO}_4)_2$	1.0 $M \text{ H}_2\text{PO}_4$	20.53†
	3.0 $M \text{ H}_2\text{PO}_4$	12.75

(c) $M/2 \text{ Fe}(\text{NO}_3)_2$ solution

ADDED REAGENT	OXIDATION		
	7 days at 11°C.	3 days at 25°C.	4 days at 30°C.
0.2 $M \text{ HNO}_3$	0.25	0.59	1.69
0.6 $M \text{ HNO}_3$	0.90	2.06	
0.1 $M \text{ H}_2\text{SO}_4$			2.21
0.45 $M \text{ H}_2\text{SO}_4$	0.59		
0.32 $M \text{ H}_2\text{PO}_4$			6.28
1.5 $M \text{ H}_2\text{PO}_4$	3.57		8.78
2.7 $M \text{ H}_2\text{PO}_4$	3.94		23.44 (complete)
0.03 $M \text{ H}_2\text{BO}_3$			0.96
0.06 $M \text{ H}_2\text{BO}_3$	0.24		
0.33 $M \text{ H}_2\text{BO}_3$			1.14
0.16 $M (\text{CH}_3\text{COOH})_2$			1.23
0.35 $M \text{ HC}_2\text{H}_3\text{O}_2$			1.27

† In these cases a precipitate formed during the experiment.

All the yellow to brown precipitates formed would seem to be basic ferric salts, but in 2(g) with magnesia the precipitate was greenish, and in series 1(c), 1(k), 2(d), and 3(b), where phosphoric acid was used, the precipitate was white (ferric phosphate?).

The $M/2$ ferrous nitrate solution would contain about 0.04 molar nitric acid and a little barium nitrate; the other ferrous nitrate solutions, made by dilution, would contain proportional amounts of these substances.

The ferrous perchlorate solution, made from iron and perchloric acid, contained a little of the free acid,—about 0.05 molar acid in the 0.25 molar solution of ferrous perchlorate and 0.02 molar acid in the 0.1 molar solution of the perchlorate.

The ferrous phosphate solution was prepared from iron and phosphoric acid; unless there is an excess of acid present a white solid (ferrous phosphate?) separates during the preparation. The 0.5 normal ferrous phosphate solution would contain 0.5 molar $\text{Fe}(\text{H}_2\text{PO}_4)_2$ and about 1.0 molar free (excess) H_3PO_4 , while the 0.2 and 0.08 normal ferrous phosphate solutions would contain proportional amounts of these constituents. These solutions form precipitates on standing, especially the two dilute solutions; addition of more phosphoric acid is necessary to prevent this precipitation. It is evident that *exact* formulation of the constituents of these solutions requires a study of the pH, etc.

Ferrous acetate solutions were prepared from ferrous sulfate and barium acetate solutions, the latter being in slight excess. This excess of barium acetate, 0.005 gram-mole per liter, is allowed for in tables 1(i) and 1(j). These ferrous acetate solutions oxidized very rapidly at room temperatures, considerable brown precipitate and scum forming within 24 hr.; this is undoubtedly due to the weakness of acetic acid. It is reported that ferrous bicarbonate solutions are oxidized similarly with the greatest readiness. The ferrous acetate solution (1(l)) had an initial pH of 2.5, which changed to 2.1 in 2 days.

Ferrous succinate solution was prepared from ferrous sulfate solution and barium succinate, but the reaction was incomplete, and the solution (1(k)) contained 0.02 mole of sulfate to 0.08 mole of succinate radical. This solution oxidized rapidly, forming much dark brown precipitate and scum; the initial pH was about 5. In the two experiments in 1(k) where free succinic acid was added, it did not dissolve completely, and the concentrations quoted are approximate.

Only the ferrous chloride solutions were titrated with potassium dichromate solution. The solutions of the other ferrous salts were titrated with potassium permanganate solution; but the solutions containing oxalic and citric acids, those of 1(m) and 1(n), were titrated with ceric sulfate solution.

EXPERIMENTS WITH OTHER SOLUTIONS

A. Ferrous chloride in alcohol

Anhydrous ferrous chloride was made; it was insoluble in ether, but freely soluble in alcohol. The solution in absolute alcohol (99 per cent by weight) turned brown rapidly in the air, but the addition of a little concentrated hydrochloric acid (aqueous solution) made the alcoholic solution a clear yellow color. The stock alcoholic solution was 0.5 molar in hydrochloric acid and 0.4 molar in ferrous chloride; the more dilute solutions were made by diluting this stock solution with alcohol. In these solutions the ferrous salt was determined by diluting with water, distilling off the alcohol in a stream of carbonic acid gas, cooling, diluting, and titrating with potassium dichromate solution.

The 0.4 molar solution of ferrous chloride in alcohol oxidized to the extent of 15 per cent in a couple of hours, and of 36 per cent in 1 day at room temperatures. With 0.4 *M*, 0.16 *M*, and 0.06 *M* solutions in alcohol the oxidation in 6 days at 11°C. was 90 per cent complete, and in the presence of extra 2 molar hydrochloric acid (aqueous) it was quite complete. Other experiments indicated that in 89 per cent (by weight) alcohol the ferrous chloride oxidized somewhat more slowly than in the 99 per cent alcohol.

Ferrous chloride thus undergoes oxidation much more rapidly in alcoholic solution than in aqueous solution. Addition of hydrochloric acid hastens the oxidation in both solvents.

B. Ferrous sulfate in concentrated sulfuric acid

Ferrous sulfate crystals were shaken with concentrated sulfuric acid for 2 days, and the solution was filtered through a porous fritted-glass plate. The resulting slightly turbid solution of ferrous sulfate in about 85 per cent (by weight) sulfuric acid was kept in a current of dry air for 4 days at 28°C. There were crystals in each sample at the end of that time, and it was therefore doubtful whether the ferrous sulfate was ever all dissolved. The original 5 cc. of solution (8.66 g.) required 1.36 cc. of *N*/10 permanganate; under the conditions stated the oxidation was equivalent to 0.24 cc. of permanganate. With the addition of phosphoric acid (90 per cent acid) to give a concentration of 0.65 molar, the oxidation was equivalent to 0.48 cc. of permanganate. Oxidation in this solvent is therefore proportionately greater than in water, and even here phosphoric acid accelerates the oxidation.

C. The oxidation of aqueous ferrous sulfate solutions in the presence of oxalic and citric acids

To prevent the oxidation of ferrous salt solutions the addition of citric acid has been proposed, but citric acid and similar acids have the power of

reducing ferric salts, especially in sunlight; moreover, the simple estimation of ferrous salts by permanganate and dichromate breaks down in the presence of these organic acids.

A drop of ferric salt solution mixed with one of oxalic acid, both $M/20$, after standing a few minutes in ordinary laboratory light, gave a blue color with potassium ferricyanide, while under similar conditions oxalic acid only slowly reduced potassium ferricyanide. With potassium permanganate solution the titration of ferrous salt in the presence of oxalic acid, even in the presence of phosphoric acid in the cold, was out of the question. With potassium dichromate solution, using potassium ferricyanide as outside indicator, the ferrous salt could be estimated in the cold with moderate accuracy, say 1 per cent, if the indications of the outside drop were observed at once, i.e., within half a minute; in a longer time the blue color appeared, since the oxalic acid then reduced the ferric salt, and light would accelerate this reduction. Thus with ferrous sulfate solution (0.0587 M) and oxalic acid (0.0837 M), in the presence of sulfuric acid (except where phosphoric acid was used), the following results were obtained:

FeSO ₄ SOLUTION	H ₂ C ₂ O ₄ SOLUTION	H ₃ PO ₄ (16 M)	KMnO ₄ TITRATION	
			Cold	Hot
			cc.	cc.
20	0	0	11.39	
0	20	0		16.24
20	20	5	(11.8)*	27.61
			K ₂ Cr ₂ O ₇ TITRATION IN THE COLD	
			cc.	
20	0	0	9.25	
20	5	0	9.25	
20	20	0	9.35	

* Fugitive.

Though cold oxalic acid solution was fairly rapidly oxidized by permanganate and ceric sulfate and only slowly by dichromate, yet the mixture of ferrous salt and oxalic acid was oxidized fairly rapidly by the dichromate, or the ferrous salt could only be approximately estimated thus in the presence of oxalic acid. Similarly, potassium dichromate oxidized ferrous salt and citric acid simultaneously, and there was no direct relation between the amount of iron oxidized and the amount of citric acid oxidized. As potassium dichromate oxidized citric acid solution very slowly in the cold, this simultaneous oxidation is an example of induced reaction, or the oxidation of ferrous salt catalyzed the oxidation of citric and oxalic acids.

Ferrous salts, however, could be titrated by ceric sulfate solution in the presence of oxalic and citric acids without appreciable error. In these titrations diphenylamine, dissolved in sulfuric acid, was used as indicator. With diphenylamine the titration must be taken to a definite purple color; too rapid a titration, too great a dilution, insufficient acid (both sulfuric and phosphoric acid), and the formation of a precipitate of ferric phosphate, all made for high results, while an excess of sulfuric acid made for a low result and a less sensitive one. Considerable care was needed to obtain consistent results with this indicator, and undoubtedly the recently introduced indicators would be better. The best results were secured in a solution which was from 0.2 to 1 or 2 molar in both sulfuric and phosphoric acid. The following results were obtained:

<i>M</i> /20 FeSO_4	<i>M</i> /20 $\text{H}_2\text{C}_2\text{O}_4$	CITRIC ACID	$\text{Ce}(\text{SO}_4)_2$ USED IN TITRATION
cc.	cc.		cc.
5	0		2.07
5	5		2.04*
5	20		2.08*†
5		1 g.	2.05
10	0		4.08
10	10		4.07
10		10 cc. of <i>M</i> /10	4.07

* This end point faded in the sunlight.

† A rapid titration gave higher results.

Using the ceric sulfate titration, experiments on the oxidation of ferrous sulfate solutions in the air in the presence of oxalic and citric acids, and in the presence and absence of light, were carried out. In series 1(m) 10-cc. samples of 0.05 molar ferrous sulfate solution, which was also 0.025 molar in ferric sulfate, were used. The experiments "in the light" were done indirectly in sunlight in the daytime and in electric light at night; those "in the laboratory" were done in diffused light in the daytime only; those "in the dark" were kept in a dark cupboard.

In series 1(n) freshly made 0.1 molar ferrous sulfate solution was used, and the oxidation was allowed to proceed at room temperatures, the mean temperature being 17°C., and in the dark; 5 cc. of the ferrous sulfate solution was used in each test. The solutions containing appreciable quantities of oxalic and citric acids, over 0.05 molar, became yellow more or less rapidly, and those containing much oxalic acid soon gave a precipitate of yellow ferrous oxalate, $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; this separation of insoluble ferrous salt decreased the extent of oxidation (see the three ex-

amples marked[†] in table 1(n)); in the fourth example (marked[†]) in the more concentrated sulfuric acid solution the precipitate only appeared towards the end of the experiment and the oxidation of the ferrous salt was not retarded.

SUMMARY

1. Phosphoric acid accelerates the oxidation of ferrous salts. When the concentration of phosphoric acid is high, the rate of oxidation slackens a little.

2. Hydrochloric acid increases the oxidation of ferrous salts. At room temperature the increase in oxidation is slight up to 1 molar hydrochloric acid, but thereafter it rises at an increasing rate; at 25°C. the influence of hydrochloric acid is more marked.

3. Sulfuric acid does not increase the rate of oxidation of ferrous salts, except that at concentrations above 18 molar the rate of oxidation is increased slightly.

4. Neutral solutions of ferrous salts are oxidized more rapidly than acid solutions (i.e., than moderately acid solutions). At 25°C. the rate of oxidation decreases from that of a neutral solution until a concentration of sulfuric acid of about 1 molar is reached, or a concentration of hydrochloric acid of about 0.5 molar. At room temperatures the rate of oxidation decreases until the acid concentration is about 0.1 molar.

5. The ferrous salts of weak acids are oxidized more rapidly than those of strong acids; e.g., there is rapid oxidation with ferrous acetate solutions, with ferrous chloride solutions buffered with borax or sodium acetate, with ferrous salt solutions containing calcite and other substances which would remove free acid.

5a. Similarly, 0.1 molar sulfuric acid prevents the rapid oxidation of ferrous acetate solutions at room temperature; the addition of acetic acid to ferrous chloride solutions containing 0.1 molar hydrochloric acid has no effect on the oxidation; boric acid behaves similarly. Sulfuric acid, and even phosphoric acid, reduces the rate of oxidation of ferrous succinate solutions.

6. Phosphoric acid may increase the rate of oxidation of ferrous salts partly because it is a relatively weak acid, but its main effect seems more specific. Phosphorous acid and hypophosphorous acid also increase the rate of oxidation. The oxidation of ferrous phosphate solutions is particularly rapid.

7. At room temperatures small concentrations of nitric acid, up to 0.5 molar, affect the rate of oxidation just as sulfuric or hydrochloric acid does, i.e., very slightly. Above this concentration the nitric acid oxidizes the ferrous salt rapidly. Nitric and hydrochloric acids together in small

concentrations (less than 0.2 molar) do not affect the oxidation. The rate of oxidation of ferrous nitrate solutions is similar to that of solutions of the chloride and the sulfate.

8. Oxides of nitrogen (from acidified sodium nitrite) rapidly accelerate the oxidation of ferrous salts. Platinum black also catalyzes the oxidation (1).

9. Neutral salts make little difference in the rate of oxidation of ferrous salt solutions. The presence of a considerable quantity of chloride increases somewhat the rate of oxidation of ferrous chloride solution.

10. No relation can be seen between the rate of oxidation and the solubility of oxygen in the various solutions; the latter must be secondary to the other factors involved. Similarly, the formation of a precipitate (generally of basic salt) in the solutions is due to low acid concentration and thus accompanies high rate of oxidation, although it does not seem to cause the latter directly.

11. The rate of oxidation (see table 3) is proportional to the square of the concentration of the ferrous salt. In table 3(a) the rate of oxidation of the $M/4$ solutions is six times that of the $M/10$ solutions, and that of the $M/2$ solution is four times that of the $M/4$ solutions (see also reference 1).

12. The addition of acid, up to a concentration of 0.2 molar, increases the rate of oxidation of the $M/2$ and $M/4$ solutions. Hydrochloric and sulfuric acids have the same effect as nitric acid; hence the experiments with the first two are not reported.

13. Oxidation of the ferrous phosphate solutions is very rapid; in 16 days at room temperatures it is about 75 per cent complete with the solutions containing the least phosphoric acid. Addition of phosphoric acid decreases the rate of oxidation for the concentrated ferrous phosphate solutions, but increases it for the dilute solutions ($M/12$). In these experiments (table 3(b)) the rate of oxidation is not proportional to the square of the ferrous salt concentration, but the exact "free acid" concentrations in these solutions are difficult to determine.

14. Addition of sulfuric, hydrochloric, or nitric acid, up to 0.2 molar, decreases the rate of oxidation of the $M/2$ ferrous phosphate solution by 20 per cent, corresponding to 16.5 instead of 20.53 cc. of permanganate (compare 5a and 21).

15. With the addition of 2.7 molar phosphoric acid the oxidation of $M/2$ ferrous nitrate solution was completed within 4 days at 30°C. (compare table 2(e)).

16. Boric, succinic, and acetic acids decrease slightly the rate of oxidation of $M/2$ ferrous nitrate solution at 30°C.; such a decrease is not noticeable in tables 1 and 2.

17. In the dark, ferric salt solution is not reduced by citric acid and is only slightly reduced by oxalic acid.

18. In the light, citric acid and oxalic acid reduce ferric salt continuously; the reduction is proportional to the concentration of these acids. In equimolar solutions the reduction by citric acid is greater than by oxalic acid.

19. Addition of sulfuric acid prevents the reduction by citric acid. Phosphoric acid accelerates the oxidation of the ferrous salt even in the presence of citric acid.

20. In the absence of light, oxalic and citric acids increase the rate of oxidation of ferrous salt solutions. The effect is slight at concentrations less than 0.05 molar, but greater at higher concentrations.

21. This effect of oxalic and citric acids is diminished by increasing the sulfuric acid concentration (see 5 and 5a).

22. In general, then, oxalic and citric acids behave as the other organic acids (weak acids), but the formation of insoluble ferrous oxalate and especially the influence of light introduce further complications with these two acids.

CONCLUSIONS

No simple or single explanation will account for the facts summarized above. In very dilute acid solutions some relation between the hydrogen ion concentration and the rate of oxidation waits to be unravelled, but in concentrated acid solutions and in non-aqueous solutions the hydrogen ions may play a minor part in the oxidation.

High rates of oxidation are undoubtedly caused by (a) specific catalysts, such as phosphoric acid, hydrochloric acid (in high concentrations), nitric acid (direct oxidizer), oxides of nitrogen, and surface catalysts such as platinum black, and (b) low acidity.

A solution of a ferrous salt undergoes the minimum oxidation in the presence of a moderate amount of a strong non-oxidizing acid, like sulfuric and hydrochloric acids; a concentration of such an acid of about 0.2 *normal* is suitable, or of sulfuric acid even up to 6.0 *normal*.

REFERENCE

- (1) POUND: J. Soc. Chem. Ind. **55**, 327T (1936).

THE OXIDATION OF SOLUTIONS OF FERROUS CHLORIDE IN ALCOHOLS

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I. EXPERIMENTS ON THE RATE OF OXIDATION OF FERROUS CHLORIDE

Anhydrous ferrous chloride, a light brown substance, was made at a red heat from iron and hydrogen chloride. Its solutions in the various alcohols were allowed to undergo oxidation either in the air or in a desiccator through which dry air was continuously aspirated. The alcoholic solutions, 5 cc. usually, were in test tubes 1 in. in diameter; after a given time the solutions were diluted with water and sulfuric acid, and then were titrated with ceric sulfate solution. The experiments were carried out at room temperatures.

The results of the chief experiments are in tables 1 and 2. In table 1 the relative ferrous salt concentrations of the solutions are given against the time in hours. The results indicate that the initial oxidation is bimolecular with respect to the ferrous salt, as it is in aqueous solutions. Table 1 gives the value of the specific speed,

$$k = -\frac{dc/dt}{c^2}$$

where c = the concentration of the ferrous salt in moles per liter (which also is the normality of the ferrous salt as reducing agent), and t = the time, in minutes, during which the oxidation has proceeded. The time, in hours, over which the constant value of k is obtained, is given immediately after k . The change in k after that period is indicated in the last column, d meaning that k has decreased, i meaning that k has increased thereafter. The experiments marked "dry" were performed in a stream of dry air; those marked "air" were performed in the open air.

Evidently the solutions of ferrous chloride in the alcohols oxidize much more quickly than its solution in water. For the aqueous solution of ferrous sulfate in the presence of 0.1 normal sulfuric acid the value of k , taken over a couple of years at an average temperature of 15°C., is 0.000,012 (1). In 87 per cent (weight per cent) ethyl alcohol with 0.01 normal hydrochloric acid the oxidation is thirty-six times faster; in methyl alcohol three hundred and eighty times and in ethyl alcohol four thousand

TABLE 1
Relative oxidation of ferrous chloride in alcoholic solutions*

SOLVENT ALCOHOL	TIME hours	TEMPERATURE °C.	AIR OR DRY†	ORIGINAL NORMALITY	k	RELATIVE AMOUNT OF FERROUS SALT REMAINING AFTER										CHARGE IN 1/4
						0 hr.	1 hr.	2 hr.	3 hr.	4 hr.	5 hr.	6 hr.	7 hr.	10 hr.	20 hr.	
1. Methyl alcohol.....	91	14	Air	N	0.071	100	98	97	95	93	92	90	88	84	72	d
2. Ethyl alcohol (87 per cent) + 0.01 N HCl.....	160	15	Air	0.153	0.0046 (30)‡	100										d
3. Ethyl alcohol (98.6 per cent)...	6	26	Dry	0.947	0.00043(20)	100	84	73	63	55	49	46		96	94	d
4. Ethyl alcohol (98.6 per cent)...	25	18	Dry	0.100	0.038 (4)	100	77	61	48	37	30	27	25	19	10	i
5. Ethyl alcohol (99.5 per cent)...	19	10	Dry	0.061 (5)	0.049 (2)	100	81	68	57	48	41	34	30	22	6	i
6. Ethyl alcohol (99.5 per cent)...	6	10	Air	0.090	0.049 (2)	100	70	52	39	30	24	20				i
7. n-Propyl alcohol.....	4	14	Air	0.090	0.094 (2)	100	58	34	22	16						i
8. Isopropyl alcohol.....	20	10	Dry	0.075	0.28 (4)	100	84	75	69	65	63	61		50	35	d
9. n-Butyl alcohol.....	2	17	Air	0.037	0.039 (2)	100	52	30								i
10. Isobutyl alcohol.....	6	14	Dry	0.029	0.41 (1)	100	62	43	29	21	17	15				i
11. tert-Butyl alcohol.....	9	29	Air	0.050	0.51 (6)	100	26									d
12. n-Amyl alcohol.....	19	11	Dry	0.056	0.65 (1)	100	69	53	42	35	30	26	23		8	
13. Isoamyl alcohol.....	3	18	Dry	0.059	0.13 (19)	100	71	54	41							i
14. Isocaprylic alcohol.....	3	12	Air	0.056	0.13 (2)	100	50	30	15							i
				0.003	4 (1)	100	50	30								i

* The oxidation of ferrous chloride in the alcoholic solutions being bimolecular, the figures and the curves for the relative amounts, r , of ferrous salt remaining after various times, t , only directly correspond to the values of k if the original solutions are of equal normality, N . In other words, all solutions which have the same original value for the product kN will give the same relative oxidations with time and the same curve for r/t . The values of k may be obtained from the given values of r , since

$$k = d \left(\frac{100 - r}{rN} \right) / dt$$

† "Air" refers to experiments performed in the open air; "dry" to experiments performed in dry air.

‡ The time, in hours, over which the constant value of k is obtained.

§ d represents a decrease in k , i an increase.

times faster; while in the higher alcohols the action is up to one hundred times faster than in ethyl alcohol.

The speed of these oxidations varies greatly with the water content of the alcohols used, with the acidity of the solutions, and probably with other factors, as is usual in chemical velocity experiments. The alcohols were dehydrated with potassium carbonate and distilled in dry systems. It was noticed that the oxidations in the open air (moist) proceeded faster than those in the desiccator (dry air),—e.g., experiments No. 5 and 6 with ethyl alcohol; with isopropyl alcohol a similar difference was noticed; with the higher alcohols the difference was similar but smaller. Other experiments indicate that water retards the oxidation, but the evaporation of the alcohols may be greater in the open air. In the experiments with dry air the volume of air in the desiccator itself was more than sufficient to oxidize the samples completely, apart from the slow current of air

TABLE 2

Values of k for oxidation of ferrous chloride in alcoholic solutions

SOLVENT ALCOHOL	k	
	In dry air	In the open air
Methyl alcohol		0.0046
Ethyl alcohol (99.5 per cent)	0.049	0.094
<i>n</i> -Propyl alcohol		0.28
Isopropyl alcohol	0.039	0.061
<i>n</i> -Butyl alcohol		0.41
Isobutyl alcohol	0.51	0.62
<i>tert</i> -Butyl alcohol		0.65
<i>n</i> -Amyl alcohol	0.13	
Isoamyl alcohol	0.13	
Isocaprylic alcohol		4

which continued during the oxidation; only in experiment No. 3 was air not present in this large excess.

The values of k in table 1 are therefore approximate; they refer to the first few hours of the oxidation. The further complications produced by the ferric salt formed and by the action of light would preclude any satisfactory value of k being found over a long period. On account of the above disturbing factors the influence of temperature on k could not be observed. The results undoubtedly indicate the faster oxidation in the higher alcohols.

II. THE INFLUENCE OF WATER ON THE OXIDATION OF SOLUTIONS OF FERROUS CHLORIDE IN ALCOHOLS

Various amounts of water were added to solutions of ferrous chloride in the different alcohols; these solutions were allowed to oxidize for a

suitable time in the open air, and the residual ferrous salt was then estimated. The results are summarized in tables 3 and 4 and in figure 1. The diminution in the rate of oxidation is most marked with the higher alcohols, and it is least with methyl alcohol. With ethyl alcohol solutions, 1 per cent of dissolved water reduces the oxidation to 80 per cent of that occurring in absolute alcohol; 2 per cent of water reduces the oxidation to 62 per cent, 10 per cent of water reduces it to 9 per cent, and 20 per cent of water reduces it to 3.5 per cent. Also, addition of alcohol, up to 50 per cent by weight, to acid aqueous solutions of ferrous chloride had no effect on the oxidation over 11 days.

The solutions of table 4(B) were made by adding small quantities of 85 per cent alcohol to the ferrous chloride solution in 99.4 per cent ethyl alcohol; the aqueous solutions with isocaproic alcohol were made simi-

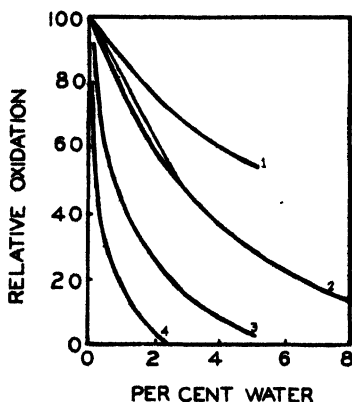


FIG. 1. Relation between the oxidation of ferrous chloride and the per cent of water in the alcoholic solutions used. Curve 1, methyl alcohol; curve 2, ethyl alcohol; curve 3, *n*-butyl alcohol; curve 4, isocaproic alcohol.

larly, for water alone was not readily soluble in that alcohol; also in the isoamyl alcohol the whole of the added water did not perhaps dissolve. In table 4 the second column gives the oxidation relative to that which, from extrapolation, would have occurred in absolute (100 per cent) alcohol; the third or last column gives the oxidation relative to the original amount of ferrous salt present. Table 4(A) indicates that the oxidation in absolute alcohol would exceed the original ferrous salt present; this perhaps indicates a more complex oxidation, which is confirmed by the gasometric experiments later. To make this presentation clear: 5 cc. of the first solution of table 4(A), ferrous chloride in 98.7 per cent alcohol, which at the start needed 1.73 cc. of 0.1035 *N* ceric sulfate solution to oxidize the ferrous salt, after 20 hr. needed 0.27 cc. of ceric sulfate solution; thus the ferrous salt oxidized in the 20 hr. was equivalent to 1.46 cc.

of ceric sulfate solution, i.e., 84 per cent of the ferrous salt was oxidized; but by extrapolation the oxidation in the 100 per cent alcohol would have

TABLE 3

Relative amounts of ferrous chloride oxidized in alcoholic solutions containing water

PER CENT WATER	(1) METHYL ALCOHOL	(2)* ETHYL ALCOHOL	(3) N-PROPYL ALCOHOL	(4) N-PROPYL ALCOHOL	(5) ISOPROPYL ALCOHOL	(6) N-BUTYL ALCOHOL	(7) ISOBUTYL ALCOHOL	(8) tert-BUTYL ALCOHOL	(9) N-AMYL ALCOHOL	(10) ISOAMYL ALCOHOL	(11) ISOCAPRYLIC ALCOHOL
0	100	100	100	100	100	100	100	100	100	100	100
1.2	85	73		63	46	44		83	68	66	(16)
2.4	72	54	50	50	24	16	37			51	(0)
4.8	56	30	37		2	4				32	
Hours.....	22	6	2	1	3	2	4	1	2	2	2
Temperature, °C..	15	18	14	18	10	17	18	29	11	12	12
Per cent†.....	30		55	39	71	66	73	89	46	35	(20)

* Column 2 is extrapolated from table 4(A).

† Per cent ferrous chloride oxidized in the 100 per cent alcohol in the same time.

TABLE 4

Relative oxidations of ferrous chloride in ethyl alcohol solutions

	WATER	OXIDATION RELATIVE TO THAT IN ABSOLUTE ALCOHOL	OXIDATION RELATIVE TO FERROUS SALT IN ORIGINAL SOLUTION
	<i>per cent</i>		
(A) 0.036 N solution; 20 hr. at 19°C.	0	(100)	121
	1.3	69	84
	3.8	46	55
	6.2	21.5	26
	8.7	11.5	14
	11.1	7.5	9
	16.0	3.5	4
(B) 0.05 N solution; 6 hr. at 18°C.	0	(100)	93
	0.6	89	82
	0.9	83	77
	1.1	79	73
	1.4	74	68
	1.6	71	66
	1.9	65	61
	2.5	53	49

been 2.1 cc. of ceric sulfate solution, so that the oxidation in the 98.7 per cent alcohol was 69 per cent of that which would have occurred in the 100 per cent alcohol. The results of tables 4(A) and 4(B) agree reasonably

TABLE 5

Effect of reagents on the oxidation of alcoholic solutions of ferrous chloride

REAGENT USED PER 5 CC. OF ALCOHOLIC SOLUTION	MOLES OF REAGENT ADDED PER LITER	MOLES OF WATER ADDED PER LITER*	RELATIVE OXIDATION IN				
			99.4 per cent ethyl alcohol			n-Propyl alcohol T†	n-Butyl alcohol
			W†	X†	Y†		
0	0	0	100	100	100	100	100
0.05 cc. water.....		0.55	57	47		61	41
0.15 cc. water.....		1.65	21				
0.30 cc. water.....		3.3	4				
0.05 cc. 96% H ₂ SO ₄	0.17	0.04	26 ^(a)	25	42 ^(b)	28	31 ^(b)
0.1 cc. 96% H ₂ SO ₄	0.36	0.09		17	33 ^(b)		
0.2 cc. 96% H ₂ SO ₄	0.72	0.18		14	23 ^(b)		
0.5 cc. 96% H ₂ SO ₄	1.7	0.45		7			
0.05 cc. 10 M HNO ₃	0.1	0.35	32				
0.05 cc. 11 M HCl.....	0.1	0.45				62	
0.075 cc. 11 M HCl.....	0.15	0.65	61			57	
0.1 cc. 11 M HCl.....	0.2	0.9		34			
0.1 cc. acetic acid.....	0.3			67			
0.02 g. boric acid.....	0.06				100		
0.05 g. boric acid.....	0.16				89 ^(c)	85 ^(c)	
0.10 g. boric acid.....	0.32			59	72 ^(c)		
0.02 g. succinic acid.....	0.03				65		
0.05 cc. 90% H ₃ PO ₄	0.17	0.09	77			88	
0.5 cc. 90% H ₃ PO ₄	1.7	0.9	59				
0.1 g. sugar.....				95 ^(c)			
Calcite.....			100	91			
0.1 g. zinc oxide.....			82				
0.1 g. magnesia.....				91			
Platinum, bright or black..			96				
0.05 cc. 1 M NaNO ₂ solution	0.01	0.5	40				
0.05 cc. 1 M NaNO ₂ solution + 0.05 cc. H ₂ SO ₄	0.01	0.55		120 ^(d)			
0.10 cc. 1 M NaNO ₂ solution + 0.05 cc. H ₂ SO ₄	0.02	1.15		200 ^(e)			
0.05 cc. 0.6 M NaOH in alcohol.....	0.006				106 ^(f)		
0.2 cc. 0.6 M NaOH in alcohol.....	0.024				100 ^(f)		

* 99.4 per cent ethyl alcohol contains 0.25 mole of water per liter; this is not included in column 3.

† Experiment W was for 116 min. at 12°C.; original ferrous chloride was 0.0874 N; blank oxidation = 50 per cent. Experiment X was for 97 min. at 13°C.; original ferrous chloride was 0.0747 N; blank oxidation = 50 per cent. Experiment Y was for 79 min. at 16°C.; original ferrous chloride was 0.1102 N; blank oxidation = 42 per cent. Experiment T was for 75 min. at 17°C.; original ferrous chloride was 0.0485 N; blank oxidation = 52 per cent.

(a) with 0.08 cc. of 96 per cent sulfuric acid; (b) with 100 per cent sulfuric acid; (c) incomplete solution of reagent; (d) trouble with titration; (e) trouble with titration and oxidation is complete; (f) precipitate formed.

closely; in table 3 columns 3 and 4 indicate the agreement of duplicate experiments.

III. EFFECTS OF REAGENTS ON THE OXIDATION OF FERROUS CHLORIDE SOLUTIONS IN ALCOHOLS

The results are given in table 5. The influence of water has been discussed. The presence of acids decreases the oxidation of the ferrous salt, strong acids having a greater influence than weak acids; the effects of water and acid are roughly additive. In contradistinction to the behavior of aqueous solutions of ferrous salts, in the alcoholic solutions phosphoric acid behaves normally and does not increase the oxidation. Platinum and basic substances do not increase the oxidation. Oxides of nitrogen, but not nitrites, do catalyze the oxidation, as they do also in aqueous solutions.

TABLE 6

Electrical conductivities of alcoholic solutions of ferrous chloride during oxidation

TIME	N	k AT 20°C.	TIME	N	k AT 20°C.
In 98.2 per cent ethyl alcohol			In 99.5 per cent ethyl alcohol		
hours		ohms per cm.	hours		ohms per cm.
0	0.1670	0.000866	0	0.1627	0.000674
20	0.1088	0.000936	17	0.1011	0.000980
47	0.0375	0.001325	43	0.0156	0.000919
96	0.0117	0.001323	66	0.0069	0.000864
In isopropyl alcohol			In isopropyl alcohol		
0	0.1053	0.000084	0	0.0567	<0.000187
49	0.0008	0.000158	0.25	0.0519	0.000197
			26	0.0367	0.000294
			116	0.0158	0.000447

IV. ELECTRICAL CONDUCTIVITIES OF ALCOHOLIC SOLUTIONS OF FERROUS CHLORIDE DURING OXIDATION

The solutions were oxidized in a current of dry air at room temperatures, and their specific electrical conductivities were determined at various times in a thermostat at 20°C. Typical results are given in table 6, where the first column gives the time in hours for which oxidation has proceeded, the second column gives the normality of the ferrous salt remaining at that time, and the third column gives the electrical conductivity (ohms per centimeter units) at that time.

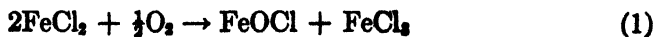
The conductivity increases with the time, i.e., as oxidation occurs, and it may become double its original value. In ethyl alcohol, after the oxida-

tion is nearly complete, the conductivity decreases slightly with further oxidation. As the change in the normality is easily followed and is more pronounced than the change in k , and as the interpretation of the latter change is beset with doubts, there seemed no reason to follow this line of work further.

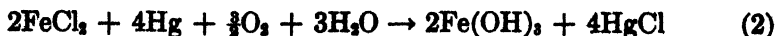
V. GASOMETRIC EXPERIMENTS

When solutions of ferrous chloride in alcohols were allowed to oxidize in known volumes of air or oxygen at room temperatures, the oxygen absorbed (i.e., the contraction in volume) was found to be greater than was expected. When the solution was placed directly over mercury in a eudiometer, the absorption of gas proceeded for months, but here the mercury reduced the ferric salt continuously and mercurous chloride was formed. Even when the solution was out of contact with the mercury the absorption of gas was two to three times greater than expected.

Some typical experiments will be described: (1) A solution of ferrous chloride in 86.3 per cent ethyl alcohol was allowed to undergo oxidation in air over mercury. The theoretical absorption ($2\text{FeCl}_2 + \frac{1}{2}\text{O}_2$) was 1.52 cc. of oxygen at N.T.P. (All the gas volumes mentioned are at N.T.P.) A fairly regular absorption of 0.1 cc. per day occurred for the first 17 days; the absorption was then slower, 0.03 cc. per day, for the next 80 days; at the 150th day 0.02 cc. was still being absorbed per day. The total absorption was 1.7 cc. in 14 days, 3.9 cc. in 100 days, 4.9 cc. in 150 days, and 5.6 cc. in 185 days. A brown precipitate appeared in the liquid in 30 days, and yellow particles of mercurous chloride were noticed in 100 days. At the end there was still a little ferrous salt in the solution and considerable acetaldehyde. If the absorption in the absence of mercury is



then absorption with the addition of the complete reaction with the mercury will be



More oxygen is absorbed than equation 2 requires; evidently some oxidation of the alcohol occurs as well.

(2) Ferrous chloride in 99.5 per cent ethyl alcohol was allowed to undergo oxidation in oxygen over mercury. The theoretical oxygen absorption was 1.65 cc. The oxidation was very rapid for 20 hr. (2.9 cc.), and then much slower. The total absorption was 3.2 cc. in 5 days.

(3) Ferrous chloride in *n*-butyl alcohol was allowed to undergo oxidation in oxygen over mercury. The theoretical oxygen absorption was 1.34 cc.

The oxidation slackened in 3 days (3.0 cc.); in 22 days the absorption was 3.6 cc. The final solution contained little or no ferrous salt, a trace of aldehyde, a brown precipitate in the body of the liquid, and a yellowish precipitate (HgCl) on the mercury. This experiment is similar to experiment 2.

(4) Ferrous chloride in 99.5 per cent ethyl alcohol in a glass tube, and not in contact with mercury, was exposed to oxygen. The theoretical oxygen absorption, corrected for the ferrous salt left at the end of the experiment, was $7.89 - 3.89 = 4.0$ cc. The oxygen absorption was regular (the gas diffused slowly into the glass tube), and the rate of absorption had not slackened at the end of 13 days when the total absorption had amounted to 5.6 cc. Acetaldehyde was present at the end of the experiment and a fruity odor was noted, which was also noticed in the oxidation experiments with the ethyl alcohol solutions in the desiccators (ethyl acetate?).

(5) Ferrous chloride in 99.5 per cent ethyl alcohol was placed over a layer of maize oil over mercury. The theoretical oxygen absorption was 3.28 cc. Rapid oxidation occurred to the second day (4.2 cc.), then regular absorption of 0.3 cc. of oxygen per day for 40 days with no sign of stopping. The alcoholic solution was uniformly brown by the fifth day (absorption = 5.2 cc.), while the maize oil was bright yellow; later the oil also became brown. Evidently the ferrous or ferric salt diffused slowly through the oil. On the 50th day the absorption was 17.7 cc. Any film of mercurous chloride on the mercury was very slight.

(6) Ethyl alcohol in oxygen over maize oil over mercury showed the very slight absorption of 0.15 cc. of oxygen in 30 days.

(7) Ferrous chloride in tertiary butyl alcohol was placed in a glass tube in the eudiometer. After 15 days at 30°C . the oxygen absorbed was 2.5 cc., and no more was absorbed in 14 more days at room temperatures; at this time the alcohol was solid. Allowing for the amount of ferrous salt left, the theoretical absorption was 2.5 cc. The initial action therefore is the simple bimolecular one.

(8) Ferrous chloride in *n*-butyl alcohol was placed in a glass tube in the eudiometer in contact with oxygen. The theoretical absorption was 5.1 cc. In 31 days 6.0 cc. of oxygen was absorbed.

(9) A solution of ferric chloride in ethyl alcohol was placed over maize oil in contact with oxygen. The oxygen absorbed was 0.2 cc. per day over a period of 8 days. The final solution contained a trace of ferrous salt and of acetaldehyde. The oxidation of ferrous chloride in ethyl alcohol and other alcohols is evidently complicated by the oxidation of the alcohols, especially as the ferric salt accumulates, though the action starts off simply as a bimolecular action.

VI. MISCELLANEOUS EXPERIMENTS

(a) A solution of ferric chloride (0.06 *M*) in 98.6 per cent ethyl alcohol after 28 days in a dark cupboard, or after 4 days in a thermostat at 30°C. in diffused light, contained no acetaldehyde and no ferrous salt.

(b) Acetaldehyde, added to such a ferric salt solution, reduced none of the ferric salt in 4 days in the dark; similar results were obtained with an aqueous solution of ferric sulfate.

(c) Ceric sulfate does not oxidize acetaldehyde quickly; or, acetaldehyde does not interfere with the titration of ferrous salt by ceric sulfate.

(d) Alcoholic solutions of ferric chloride are rapidly reduced by shaking with mercury; aqueous solutions are similarly reduced.

(e) In the presence of sunlight, alcoholic ferric chloride solution is rapidly reduced and acetaldehyde is formed. (Acetaldehyde was detected, and roughly estimated, by Schiff's reagent,—a method having limitations.) In the above solution on exposure to sunlight for 22 hr., 40 per cent of the ferric salt was reduced; when air was above the solution the reduction was a little less than when carbonic acid gas only was present. Another solution in sunlight for 9 hr. suffered 80 per cent reduction. This action has been much investigated (2). It was confirmed that the action in sunlight was of zero order, i.e., independent of the concentration of the ferric chloride; also that water (1 to 2.5 per cent) increased the reduction (up to 10 per cent), and that concentrated hydrochloric acid solution (1 to 2.5 per cent) decreased the reduction (up to 20 per cent). In the presence of air the ferrous salt obtained is (naturally) less, but the acetaldehyde (etc.) may be the same.

(f) Alcoholic ferric chloride solution on slow distillation gave acetaldehyde in the distillate and a little ferrous salt in the residue. The solution, refluxed for an hour and then distilled, produced more acetaldehyde and more ferrous salt (6 per cent reduction). Some unknown acid was also present in the distillate.

Thus the action between ferric chloride and ethyl alcohol is negligible in the dark or in diffused light, is slow at the boiling point, and is rapid in sunlight at room temperatures.

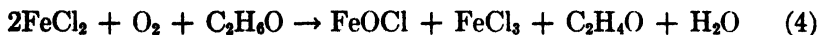
(g) In one series of experiments on the rate of oxidation of ferrous chloride in ethyl alcohol the solutions were tested at intervals for acetaldehyde. The results indicate that the aldehyde appeared only when the oxidation had proceeded to the extent of 80 or 90 per cent and that the aldehyde was formed more rapidly after that stage. These tests, involving the quantitative use of Schiff's reagent in the presence of many other substances, must be regarded as approximate.

Thus oxidation of the ferrous salt (equation 1) is the primary action; it is followed by the oxidation of the alcohol, the ferric chloride acting as a

catalyst, i.e., being reduced and reoxidized at a relatively constant rate. This last action is certainly complex, but it may be presented simply as:



This last action would continue indefinitely or until the presence of water slackened the action either directly or by favoring precipitation of the iron as basic ferric salt. However, there may be some simultaneous oxidation of the ferrous salt and the alcohol, as



and this action may occur even from the start. The production of water, according to equation 3 or equation 4, would explain the increase in electrical conductivity and the decrease in the rate of reaction with time. The latter feature is not marked with the higher alcohols. Against reaction 4 is the fact that some of the alcohols used are not easily oxidized, and yet the oxidation of the ferrous salt is rapid.

The behavior of ferrous chloride with methyl alcohol is probably akin to that with ethyl alcohol, but with the higher alcohols the iron compounds precipitate more easily and the secondary reactions may be less prominent. The rapid rate of oxidation of ferrous chloride in alcohols may be connected with the continued neutrality of the solutions; the aqueous solutions readily become acid, owing to hydrolysis of the ferric salts, and thus the rate of oxidation slackens.

VII. NOTES ON THE EXPERIMENTS

The solubility of ferrous chloride decreases as the molecular weight of the alcohol rises. The solutions of table 1 are roughly saturated, except for the methyl and ethyl alcohol solutions. These solutions are originally pale yellow or greenish yellow, and become browner as oxidation proceeds; with the higher alcohols the solutions become turbid brown. The solution of ferrous chloride in isobutyl alcohol gave an immediate brick-red suspension, which did not entirely clear on filtering through a porous glass plate. Most of the solutions were filtered thus in an atmosphere of dry hydrogen.

The isoamyl alcohol used was isobutylcarbinol, b.p. 131.5°C. The isocaprolic alcohol, b.p. 178°C., was 2-octanol or methylhexylcarbinol. The solubility of ferrous chloride in this alcohol was so slight that the results are approximate.

Preliminary experiments proved that ferrous chloride may be estimated in the presence of alcohols by titration with ceric sulfate solution. Diphenylamine or *N*-phenylanthranilic acid, dissolved in concentrated sulfuric acid, was used as indicator. The second indicator is perhaps the more sensitive. The titration proceeds normally in the presence of 50

per cent alcohol, but it is better to keep the alcohol concentration less than this. The average solution to be titrated contained 5 cc. of the alcoholic solution of ferrous chloride, 5 cc. of water, 5 cc. of 10 *N* sulfuric acid, and 2 cc. of concentrated phosphoric acid. With less acid, and with hydrochloric acid instead of sulfuric acid, the end point is less sensitive. With a greater proportion of alcohol the salts may precipitate out during the titration, again making the end point less sensitive; in these cases the results tend to be high. Those alcohols which readily separated from the aqueous solution were kept emulsified by shaking; these titrations were therefore more tedious and more likely to be overshoot, but back-titrations with ferrous chloride solution could be used to check these end points. In the presence of the alcohols the end points faded with time, but not fast enough to affect the titration.

VIII. SUMMARY

Solutions of ferrous chloride in alcohols are oxidized in air or oxygen much more quickly than the aqueous solution; in all these solvents the action is bimolecular with respect to the ferrous salt concentration. As the molecular weight of the alcohol increases, the rate of such oxidation increases, and the solubility of the ferrous chloride decreases.

Water and acids decrease rapidly the oxidation in these alcoholic solutions, this decrease being more prominent with the solutions in the higher alcohols.

The electrical conductivities of the alcoholic solutions increase during the oxidation.

The oxidation of ferrous chloride in alcohols is complicated by the oxidation of the alcohol to the aldehyde, either by the action of the ferric salt on the alcohol or by the simultaneous oxidation of ferrous salt and alcohol under influence of the ferric salt. More oxygen is used than would be expected from a normal oxidation,—in some experiments two to three times as much oxygen. The presence of light, mercury, water, and acids also affects these actions.

The author wishes to thank Mr. E. Crimmins for helping in this work and The Shell Oil Co. (Australia) for donating the tertiary butyl alcohol.

REFERENCES

- (1) POUND: *J. Soc. Chem. Ind.* **55**, 327T (1936).
- (2) PRASAD AND COWORKERS: *J. Indian Chem. Soc.* **8**, 489 (1931); **10**, 91, 101 (1933).

ANOMALOUS DIFFUSION OF QUINONE IN SALT SOLUTIONS

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In previous investigations (1, 2) anomalies of diffusion were observed that were at first not readily explained. Quinone diffused in pure water according to Fick's law with a well-defined diffusion coefficient, agreeing with the value that could be derived from the molecular weight, but if the quinone were allowed to diffuse in a uniformly distributed salt solution, for instance, in a solution of potassium sulfate, diffusion proceeded so irregularly that no constant could be determined. The well-known method of Oehlm and a similar one were used. In both, the solution of quinone was covered with a solution of the same composition but free of quinone, and after a certain time the column of liquid was carefully divided into layers which were analyzed. The characteristic anomaly in the salt solutions consisted in the appearance of too large amounts of quinone in the top layers of the column. It seemed as if a convection current had started and had transported some of the quinone solution upward. The density gradient at the outset was correct, i.e., the liquid above was distinctly less dense than the quinone solution below.

G. S. Hartley (3) suggested that this behavior might be due to the following mechanism: A uniformly distributed solute could show a so-called "diffusion rétrograde," i.e., it might become unequally distributed if a second solute were allowed to diffuse in the liquid, the unequal distribution occurring mainly where the concentration gradient was steep near the juncture of the two solutions. This may result from a general type of Donnan effect. Owing to a mutual change in solubility, the potassium sulfate in the quinone solution develops other forces than in pure water, and these fields of force produce an unequal distribution of the potassium sulfate. This unequal distribution of the potassium sulfate, occurring during the process of diffusion, may cause an inadmissible density gradient, although the latter started out correctly. Thus, a thin layer of the liquid at the junction of the two solutions becomes less dense than the solution above. This irregular density gradient may produce convection currents, which disturb the normal process of diffusion. The correctness of this

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explanation was proved by reducing the concentration of the pure potassium sulfate solution above to a sufficiently marked degree so that it was less dense than the solution of potassium sulfate and quinone below. The anomalies then disappeared.

It was not proved by analysis that the uniformly distributed solute actually changed its concentration near the borderline of the two solutions, owing to the diffusion of the second solute. Under the conditions of the experiments mentioned this would have been difficult to do, because it would have meant the determination of a small change in the concentration of a concentrated solution of a salt such as potassium sulfate. Since the effect is due to a mutual change in the solubility of the solutes, it should be possible to interchange them. If the quinone is uniformly distributed at the outset, and potassium sulfate is diffusing, owing to a strong concentration gradient, a change in the distribution of the quinone should be observed near the junction of the two solutions. Quinone can be determined very exactly by an iodometric method (7), hence it was likely that a change in its distribution might be determined. This direct proof appeared to be desirable, since experiments on "diffusion *rétrograde*" have been performed infrequently (3, 6).

The following experiments were done under conditions similar to those described previously (2) (cf. Tables III to IX). In the first of the previous papers it was found that potassium chloride, in contrast to potassium sulfate, showed a less marked anomaly of diffusion. In the first experiments the concentration of quinone was rather small, 27.8 millimoles per liter. In parallel experiments potassium chloride and potassium sulfate, both about 1 normal in a solution of quinone (27.8 millimoles per liter), diffused into an aqueous solution of quinone, also containing 27.8 millimoles per liter. Diffusion was allowed to go on only for a short time, as long as no salt had permeated to the top of the diffusion cylinder; hence the concentration gradient on the borderline of the two solutions always remained steep. The results are given in table 1.

There was no change in the distribution of the quinone when potassium chloride was diffusing, but a very distinct change was observed with potassium sulfate. The quinone had a tendency to pass out of the potassium sulfate solution and to accumulate in the aqueous solution; hence there was a decrease in the quinone concentration just below the liquid junction and an increase above.

At a somewhat higher concentration of quinone—55.6 millimoles per liter—a change of concentration was also shown in the presence of a concentration gradient of potassium chloride, as was to be expected. The concentration of the salt was 1 normal. Two experiments gave similar results; the results of one experiment are shown in figure 1. Here the distribution of the diffusing salt is also represented, and the decrease

of the quinone concentration below the junction and the increase above are seen clearly. The abscissae are the layers of the column of diffusion. The ordinates on the left-hand side refer to the continuous lines representing the concentration of potassium chloride, in per cent of the original concentration; the ordinates on the right-hand side refer to the dotted

TABLE 1

*Diffusion of potassium chloride and potassium sulfate in a 0.0278 normal solution of quinone**

$\tau = 11.5$ hr.; $t = 19.1^\circ\text{C}$.

LAYER†	DIFFUSION OF POTASSIUM CHLORIDE $h = 0.75$ cm.; $c = 1$ mole per liter AMOUNT OF QUINONE TITRATED‡	DIFFUSION OF POTASSIUM SULFATE $h = 0.70$ cm.; $c = 0.94$ equivalent per liter AMOUNT OF QUINONE TITRATED
33-25	5.37	5.52
25-20		
20-15	5.34	5.50
15-10	5.37	
10-5	5.38	5.54
5-0	5.39	5.41
0-5	5.37	5.24

* h = height of the layer; τ = duration of diffusion; t = temperature; c = initial concentration of the salt solution.

† 0 indicates the borderline of the two solutions; 33-25 indicates the top layer.

‡ Cubic centimeters of a 0.02 normal solution of thiosulfate needed for 2 cc. of quinone solution.

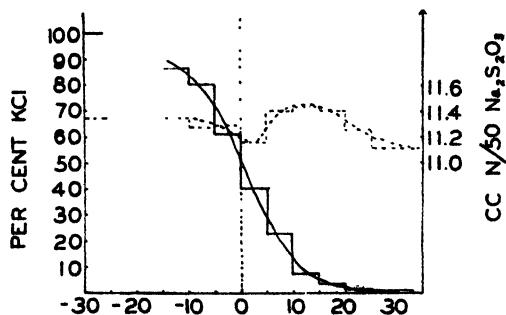


FIG. 1. Concentration gradient of potassium chloride; quinone uniformly distributed. $h = 0.80$ cm.; $\tau = 11.5$ hr.; $t = 25.6^\circ\text{C}$; c (potassium chloride) = 1 normal; c (quinone) = 0.0556 molar. —, potassium chloride; ·····, quinone.

lines, which indicate the concentration of quinone given in cubic centimeters of a 0.02 normal solution of thiosulfate needed for titrating 2 cc. of the liquid in the diffusion column.

The results with potassium sulfate were confirmed by four further experiments (two groups of two parallel experiments). They were done with special care, using the smaller concentration of quinone (27.8 milli-

moles per liter). The experiments of the first group will be discussed more fully. Pure quinone and potassium sulfate were used. The aqueous solution and the one containing salt had exactly the same concentration of quinone. Two cubic centimeters of the solutions needed 5.65 and 5.66 cc., respectively, of a 0.02 normal solution of thiosulfate for titration. Table 2 gives the complete results of one experiment in this group; the

TABLE 2

Diffusion of potassium sulfate in a 0.0278 normal solution of quinone
 $h = 0.70$ cm.; $\tau = 10$ hr.; $t = 21.8^\circ\text{C}$.; $c = 1$ equivalent per liter

LAYER	AMOUNT OF QUINONE TITRATED	
	Actual determinations	Mean value
33-15	5.58; 5.58; 5.59	5.58
15-10	5.72; 5.69	5.70
10-5	5.77; 5.74	5.75
5-0	5.64; 5.61	5.62
0-5	5.48; 5.45	5.46
5-10	5.45; 5.40	5.42
10-15	5.54; 5.56	5.55
15-20	5.64; 5.61	5.62
20-25	5.64; 5.66	5.65
25-30		Constant

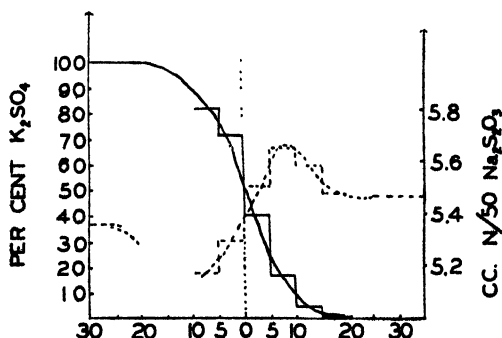


FIG. 2. Concentration gradient of potassium sulfate; quinone uniformly distributed. $h = 0.70$ cm.; $\tau = 10$ hr.; $t = 22.4^\circ\text{C}$.; c (potassium sulfate) = 0.827 normal; c (quinone) = 0.0278 molar.

second was in good agreement, and both confirmed the results given in table 1.

In figure 2 the results of an experiment of the second group are given in a manner similar to figure 1. Again the distribution of the diffusing salt was determined, and the decrease in concentration of quinone below the junction and the increase above were very marked. The difference between the highest and lowest value of the quinone concentration observed

was 6.1 per cent of quinone (table 2). For the second experiment of this group with potassium sulfate it was found to be 5.7 per cent. In the experiments with potassium chloride the corresponding differences in quinone were 2.7 per cent (*cf.* figure 1) and 2.3 per cent, respectively.

It is obvious that a similar change in distribution must occur if quinone diffuses in a solution of potassium sulfate, the salt being uniformly distributed at the outset, and that this effect may cause the disturbing anomalies previously investigated. To a minor degree this also holds for the diffusion of potassium chloride.

Some experiments with uniformly distributed succinic acid in a field of diffusion of sodium chloride and potassium chloride, respectively, were in good agreement with these results. According to Linderstrøm-Lang (5)

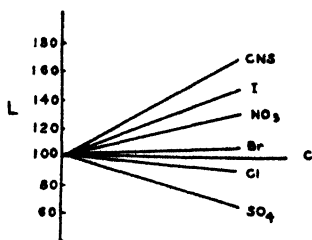


FIG. 3

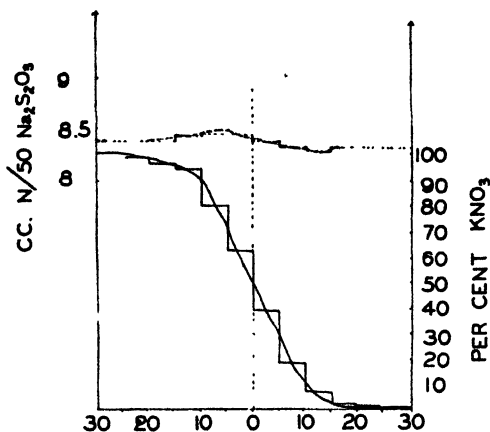


FIG. 4

FIG. 3. Relative solubilities of quinone in salt solutions. The solubility of quinone in water is taken as 100.

FIG. 4. Concentration gradient of potassium nitrate; quinone uniformly distributed. $h = 0.70$ cm.; $\tau = 11.5$ hr.; $t = 21.5^\circ\text{C}$.; c (potassium nitrate) = 1.5 normal; c (quinone) = 0.0833 molar.

the solubility of succinic acid is reduced more strongly by sodium chloride than by potassium chloride. We found a distinct shift of concentration of the succinic acid with sodium chloride and a smaller one with potassium chloride, both in the same direction as in the preceding experiments with quinone, i.e., an increase in concentration on the water side and a decrease on the salt side of the borderline. The original concentration of the succinic acid was 254 millimoles per liter and that of the salt solutions was 2 moles per liter; the temperatures were 20.9° and 20.1°C ., respectively.

As was mentioned above, we must assume the forces affecting the solubilities of the solutes to be the cause of this phenomenon. If this be so, it may be expected that substances which increase the solubility of quinone should produce a shift of concentration of the quinone in the

opposite direction, i.e., an increase on the salt side and a decrease on the water side of the borderline. Kruyt and Connar Robinson (4) have investigated the salting-out and salting-in effects of a number of salts upon quinone. Some of their results are represented in figure 3; the abscissae are the salt concentrations, c , in moles per liter, and the ordinates are the solubilities of quinone, L , on a relative scale, the solubility in pure water being taken as 100.

Obviously we might expect particular strong effects in the opposite direction for potassium thiocyanate and potassium iodide, but both have a

TABLE 3

Diffusion of potassium nitrate in a 0.0833 normal solution of quinone

$h = 0.70$ cm.; $\tau = 11.5$ hr.; $t = 21.5^\circ\text{C}$.; $c = 1.5$ moles per liter. The solution in the diffusion column contained 0.01 mole of hydrochloric acid per liter

LAYER	AMOUNT OF QUINONE TITRATED		POTASSIUM NITRATE CONCENTRATION IN PER CENT OF ORIGINAL CONCENTRATION
	Actual determinations*	Mean value	
30.6-25	8.30; 8.31	8.305	1.0
25-20			1.9
20-15	8.30; 8.32	8.31	2.5
15-10	8.30; 8.27; 8.27; 8.29	8.28	7.1
10-5	8.30; 8.31	8.305	18.7
5-0	8.36; 8.37	8.365	38.5
0-5	8.44; 8.44	8.44	62.8
5-10	8.41; 8.46	8.435	79.8
10-15	8.42; 8.43	8.425	94.0
15-20	8.37; 8.38	8.375	95.9
20-25			98.3
25-30	8.39; 8.35	8.37	

Amount of quinone titrated in original aqueous solution, 8.35, 8.34;
mean value, 8.345

Amount of quinone titrated in original potassium nitrate solution, 8.38, 8.40;
mean value, 8.39

* Cubic centimeters of a 0.01 normal solution of thiosulfate needed for 1 cc. of quinone solution.

certain tendency to react with quinone and can therefore not be used. Potassium nitrate seemed to be the most hopeful substance, since it caused a considerable increase in solubility of the quinone without tending to react in any marked degree. The first experiment gave a small effect in the direction that had been expected, but it was not quite satisfactory. Titration values of the same layer did not agree as well as desired. A second experiment was done with special care. The potassium nitrate solution was 1.5 normal, and both the salt and the aqueous solution were 0.01 normal as to hydrochloric acid, quinone being more stable in weakly

acid solutions (5). The quinone concentration was somewhat higher than in the previous experiments,—namely, 83.3 millimoles per liter. The samples were taken with carefully standardized 1-cc. pipets having a particularly good outflow. This experiment showed beyond doubt (*cf.* table 3 and figure 4) that again the uniformity of distribution of the quinone was disturbed by the diffusing salt, but now, as had been expected, in the opposite direction, as an increase in the concentration of quinone was found on the salt side of the borderline and a decrease on the water side.

Figure 4 corresponds to figure 1 and figure 2. The quinone concentration is given in cubic centimeters of a 0.01 normal thiosulfate solution needed to titrate 1 cc. of the liquid in the diffusion column.

The total quinone content was found to be unaltered after diffusion had taken place, indicating that there had been no chemical reaction.

Probably no simple correlation exists between the shifts in concentration of the quinone and succinic acid, respectively, and the absolute values in the change of their solubilities caused by the salts. The change in solubility would hardly allow us to predict unambiguously the amount of transported molecules of quinone and water caused by the diffusion gradient of the salt.

It is believed that an inadmissible density gradient and hence disturbing convection currents may occur more probably with potassium nitrate as a diffusing salt, where there is, passing from below to above, a maximum-minimum distribution of the organic solute than in the other cases, where the distribution is a minimum-maximum one, because just above the junction, in a zone containing practically nothing but the organic solute, the concentration of the latter will decrease in the case of a maximum-minimum distribution. This zone, therefore, would become less dense than the layers above containing the same solute in higher concentration. An inadmissible density gradient will not be so easily set up when the organic solute is accumulated above the liquid junction. It appears that there is a difference in this direction in these experiments. The distribution of the salt was determined gravimetrically. In the experiments with potassium sulfate, as shown in figure 2, the top layers contained no salt, as should be expected for normal diffusion in such a short time. With potassium nitrate, however, an appreciable amount of salt was found in the upper layers. It amounted to about 1 per cent in the top layer and increased to 1.9 per cent in the second layer from the top. This indicated an anomalous diffusion, i.e., one disturbed by convection currents.

The occurrence of convection currents in the case of potassium nitrate would tend to level the changes in concentration of the organic solute and thus make them less distinct. This was probably the reason why it was found much more difficult to discover a case of maximum-minimum distribution than distributions in the opposite direction.

SUMMARY

1. It was shown by direct analysis that if salts (potassium chloride, potassium sulfate, sodium chloride) diffuse in an aqueous solution of a second solute (quinone, succinic acid), the latter being uniformly distributed at the outset, the second substance changes its distribution in the region where the concentration gradient of the salt is steep. We are dealing with the phenomenon of "diffusion rétrograde."

2. If the solubility of the second solute is decreased by the salt, as is the case, for instance, with quinone and potassium sulfate, then we find a decrease of quinone concentration on the salt side and an increase on the water side of the borderline. A shift of concentration in this sense was observed with quinone in solutions of potassium chloride and potassium sulfate, and with succinic acid in solutions of sodium chloride and potassium chloride. The stronger reduction of the solubility of quinone by potassium sulfate, as compared with that by potassium chloride, corresponds to a greater shift in concentration caused by potassium sulfate; accordingly there was also a greater shift of concentration caused by sodium chloride, as compared to potassium chloride, in the case of succinic acid, the solubility of which is reduced more strongly by sodium chloride.

3. If the solubility of the second solute is increased by the salt, as is the case with quinone and potassium nitrate, the shift in concentration has the opposite sense: there is an increase in quinone concentration on the salt side and a decrease on the water side of the borderline.

REFERENCES

- (1) FREUNDLICH, H., AND KRÜGER, D.: *Z. Elektrochem.* **36**, 305 (1930).
- (2) FREUNDLICH, H., AND KRÜGER, D.: *Trans. Faraday Soc.* **31**, 906 (1935).
- (3) HARTLEY, G. S.: *Trans. Faraday Soc.* **27**, 10 (1931).
- (4) KRUYT, H. R., AND ROBINSON, CONMAR: *Koninkl. Akad. Wetenschappen Amsterdam* **29**, 1244 (1926).
- (5) LINDERSTRØM-LANG, K.: *Compt. rend. trav. lab. Carlsberg* **15**, No. 4 (1924).
- (6) THOVERT, J.: *Ann. phys.* [9] **2**, 369 (1914).
- (7) VALEUR, A.: *Compt. rend.* **129**, 552 (1899).

ULTRACENTRIFUGAL ANALYSIS AND STABILITY IN PROTEIN SYSTEMS¹

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The molar friction constant of proteins determined in ultracentrifugal analysis may be modified in the presence of water by variations in the hydrogen-ion, electrolyte, and protein concentration of the solution, by the addition both of amides, amino acids, and other chemicals and of other proteins, by heat, by ultraviolet light, by ultrasonic waves, etc.

It is important to understand the cause of such modifications in the sedimentation behavior of the dissolved unit. In some cases the effect is due to a real dissociation, but it must be recognized that in other instances it may arise from a change in the shape of the molecule, or even from a change in the degree of solvation. In extreme cases sedimentation velocity may be modified by orientations of the molecular kinetic unit.

In this study of protein stability in solution we shall (1) make the attempt to analyze the result of solvent change in influencing sedimentation and diffusion constants by setting up simple relationships between molecular weight, sedimentation constant (s), diffusion constant (D), and the Svedberg dissymmetry factor (f/f_0), (2) give representative experimental data to show how these constants are modified by the dissociation of dissolved units, and (3) consider other systems for which changes in molecular form rather than actual dissociation may be responsible in part for observed differences in molar friction constant.

I. MATHEMATICAL RELATIONSHIPS

It will be convenient for the discussion following to have at hand certain relationships between molecular weight, M , sedimentation constant, s , diffusion constant, D , and dissymmetry number, f/f_0 .

The frictional resistance to sedimentation of a spherical molecule is

$$f_0 = 6\pi\eta N \left(\frac{3VM}{4\pi N} \right)^{1/3} = k_0 \sqrt[3]{M}$$

¹ Presented at the Sixteenth Colloid Symposium, held at Stanford University, California, July 6-8, 1939.

In this expression η is the coefficient of viscosity of the solvent and V is the partial specific volume of the solute. The corresponding quantity for a molecule of any non-spherical form is

$$f = k_1 \frac{M}{s} = \frac{RT}{D}$$

The condition that f/f_0 remains constant gives

$$\frac{M^{2/3}}{s} = \text{constant} \quad (1)$$

From kinetic theory

$$kT = \frac{M}{2} v^2$$

If the temperature remains constant, the velocity of the particle increases with $1/\sqrt{M}$.

Also,

$$D = \frac{k_2}{\sqrt{M}} = \frac{RT}{k_1} \frac{s}{M}$$

therefore

$$s/\sqrt{M} \text{ is constant} \quad (2)$$

Since both conditions can not be fulfilled at the same time, either the partial specific volume must change or the shape factor must change.

The Svedberg formula for the molecular weight of a molecule in terms of s and D is

$$M = \frac{s}{D} \cdot \frac{RT}{(1 - V\rho)}$$

From its derivation this equation is valid strictly only for systems of two components. It will be correct in a three-component system in which no combination can occur between protein and any component. In the discussion to follow, we must assume no serious difficulty from this source in isoelectric dilute salt solutions when the major extra component is electrically neutral.

In the case of a sphere, we have

$$M = \frac{s_0}{D_0} \cdot \frac{RT}{(1 - V\rho)} = s_0 \sqrt[3]{M} \cdot k_2$$

which gives $s_0 = kM^{2/3}$. Further,

$$D_0 = D \frac{f}{f_0}$$

and M is a function of s/D alone. Therefore, $s \times f/f_0 = s_0$. By definition,

$$D_0 = \frac{RT}{6\pi\eta N \left(\frac{3VM}{4\pi N} \right)^{1/3}}$$

and

$$k_s = \frac{6\pi\eta N \left(\frac{3V}{4\pi N} \right)^{1/3}}{(1 - V\rho)} = \frac{1}{k''}$$

Now, inserting the values for D_0 and s_0 , we have

$$D = \frac{k'}{\sqrt[3]{M}} \cdot \frac{f_0}{f}$$

and

$$s = k'' M^{2/3} \cdot \frac{f_0}{f}$$

The ratio $f_0/f \leq 1$. Thus, if M decreases, one factor of D increases and the other decreases, while both factors in s decrease. Therefore, s will decrease while D may increase, remain constant, or even decrease as a molecule dissociates. On the other hand, if M remains constant and the protein unfolds, both s and D will decrease.

II. DISSOCIATION PHENOMENA

There are now a number of cases in which a dissociation of the protein in the system is well established. The following sedimentation and diffusion data for hemoglobin and phycocyan are sufficient to show that in these systems such a reaction takes place. In table 1 the ratios of s/D are used to calculate the molecular weight of the dissociated molecule, the dissymmetry factor (f/f_0) is calculated from the observed diffusion constant, and its sedimentation constant is calculated from the ratio

$$\frac{s}{s_1} = \frac{M^{2/3}}{M_1^{2/3}} \frac{(f/f_0)}{(f/f_0)_1}$$

The values of s and D are always corrected to the basis of a process taking place in pure water at 20°C.

In making calculations for the ratio of major to minor axis from dissymmetry number data, use has been made of recent theoretical work of Perrin. Of course molecular dimensions can be calculated with a knowledge of molecular weight, density, and dissymmetry number, but we have

preferred not to do this for three reasons: (1) Values of the dissymmetry number are limited in accuracy, because the two friction constants from which they are obtained are subject to some error. The accuracy of a determination of s is 2 to 3 per cent, of D 2 to 3 per cent, and therefore the error is from 5 to 10 per cent for the molecular weight. Thus there is some uncertainty in the evaluation of f_0 . Further, values of the friction coefficient, f , may be subject to error, because for long molecules the specific sedimentation rate may be a function of concentration. Limiting extra-

TABLE 1

Sedimentation and diffusion data for phycocyan and hemoglobin systems

A. Molecular weight data for phycocyan and its dissociation product. Normal molecule in aqueous buffer solution with pH 2.5 to 6. Dissociation product in aqueous buffer solution with pH 7 to 8.5. (Eriksson-Quensel: *Biochem. J.* **32**, 585 (1938))

	NORMAL MOLECULE	DISSOCIATED MOLECULE	
		Experimental	Calculated
M	273,000	146,000	131,000
$s_{20} \times 10^{13}$	11.4	6.2	6.1
$D_{20} \times 10^7$	4.05	4.6	
f/f_0	1.2		1.35
b/a	1:4		1:8

B. Molecular weight data for hemoglobin and its dissociation product. Normal molecule in ordinary aqueous buffer solution. Dissociation product in 40 per cent aqueous urea solution. (Steinhardt: *J. Biol. Chem.* **123**, 543 (1938))

	NORMAL MOLECULE	DISSOCIATED MOLECULE	
		Experimental	Calculated
M	76,000	38,000	43,700
$s_{20} \times 10^{13}$	4.6	3.2	3.23
$D_{20} \times 10^7$	6.3	7.7	
f/f_0	1.20		1.18
b/a	1:4		1:4

polated values of sedimentation constant for zero concentration must be used in this evaluation. (2) Values of f/f_0 are influenced by hydration by an unknown amount. (3) There is no particular justification for the assumption of the form of an ellipsoid of revolution for protein molecules.

The data are presented in a single table (table 1) for comparison, because in one case a pronounced change in s is accompanied by practically no change in D , but in the other a decrease in s and an increase in D go together. Also, the dissymmetry number for phycocyan indicates change on dissociation of the ratio of major to minor axis from 4:1 to 8:1, suggest-

ing cleavage along the major axis, but, although it is difficult to understand, there is no apparent modification of dissymmetry number for the dissociated hemoglobin.

Other interesting dissociation phenomena are found in the case of the hemocyanins, where the stability diagrams are markedly influenced by the hydrogen-ion concentration of the solution. Observations of sedimentation velocity and diffusion prove that the protein contains only one component at the isoelectric point in the case of *Helix pomatia* and *Helix nemoralis*, while the hemocyanins of *Helix arbustorum* and *Helix hortensis* contain two components in the isoelectric region. As the pH of the solution is decreased or increased, points are reached where a small change in pH causes a pronounced change in the protein. Thus, the original molecule of *Helix pomatia* (molecular weight 6,750,000) dissociates stepwise into homogeneous half, eighth, and sixteenth components. The presence of certain ions, particularly Ca^{++} and Mg^{++} , causes important changes in the stability of this system. It is important to note that the molecular weights of the hemocyanin molecules found in the blood of a certain species are always simple multiples of the lowest well-defined component. In most cases the components of the species are interconnected by reversible dissociation-association reactions which depend upon the pH value of the solution.

III. COMPLEX EQUILIBRIA

The changes in molar friction constant for the proteins considered in the preceding section are due to dissociation reactions. With other systems similar modifications of sedimentation diagrams and molar friction constant are observed, but the interpretation is more difficult to understand. In some cases changes in the molecular weight of a protein are believed to be responsible for modified sedimentation diagrams, but in others it appears that a change in the shape of the sedimenting unit is responsible for the observed effects.

As typical of cases where molecular weight changes are believed to be involved, we cite experiments of McFarlane (4) and of Pedersen (5), in which the presence of another protein of lower molecular weight, a protamine, or an amino acid causes the amount of the substance of higher molecular weight to decrease and to be replaced by a slower sedimenting component, although the protein of higher molecular weight is perfectly stable under the same conditions when it is present alone except for the salt used to repress the Donnan effect. The action of the dissociating compound on a protein is highly specific, and the magnitude of the effect varies greatly from protein to protein. Pedersen writes, "From the experi-

ments above we may conclude that in a mixture of two proteins, the smaller one may often cause transformations in the one with the larger molecules in such a way that new molecules of different size are formed.

"In the cases here investigated the new molecules were probably formed by dissociation, as they were generally smaller than the ones from which they were produced. In the mixtures with protamines, the protein and its dissociation product in some cases combined with the protamine. When the sedimentation constants for the components were not too close together, the sedimentation diagram always gave regular curves, indicating

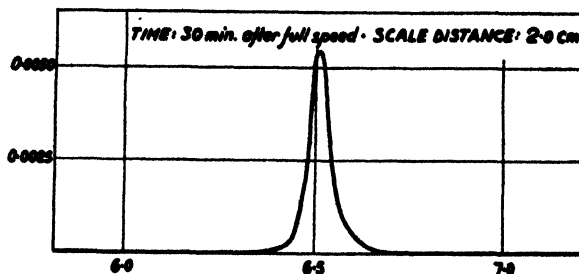


FIG. 1. Sedimentation diagram for native thyroglobulin in salt solution

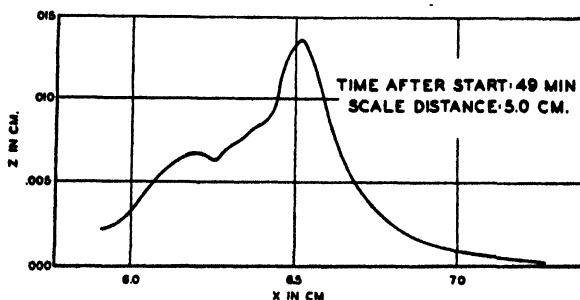


FIG. 2. Sedimentation diagram for denatured thyroglobulin in salt solution

that the new molecules formed had a definite size (and composition) and that they probably "obeyed" the Svedberg multiple law."

More recently it has been found in this Laboratory that changes in sedimentation behavior of the general type mentioned above can be produced in solutions of a number of uniform proteins, by the simple expedient of reducing the electrolyte content, even within the usual limits of pH stability (3). Thus, the same kinds of transformation in sedimentation diagrams are produced without the addition of any reagent whatsoever, and we shall give reasons for believing these changes in sedimentation behavior to be due to an unfolding of the original molecular kinetic unit.

Native thyroglobulin sediments in salt solution within its pH stability region (pH 3 to 11.3) as a single well-defined protein (figure 1) ($s_{20} = 19.2$

$\times 10^{-12}$; $M = 650,000$). Furthermore, it appears appreciably stable in electrolytes, becoming somewhat less homogeneous on long standing, as judged from the sharpness of the boundary on sedimentation.

When the protein is denatured in salt solutions by heating, by ultra-violet light, or by acid, it becomes polydisperse, the boundary being spread over a considerable distance in the centrifuge cell, presumably indicating dissociation and aggregation (figure 2).

When the protein is brought outside the pH stability region in salt solutions, well-defined slower sedimenting boundaries are present, indicating a dissociation of the protein. Thus thyroglobulin behaves as a typical protein in the electrolyte solutions.

Studies with electrolyte-free solutions of this protein have revealed profound changes in the sedimentation behavior within the usual pH sta-

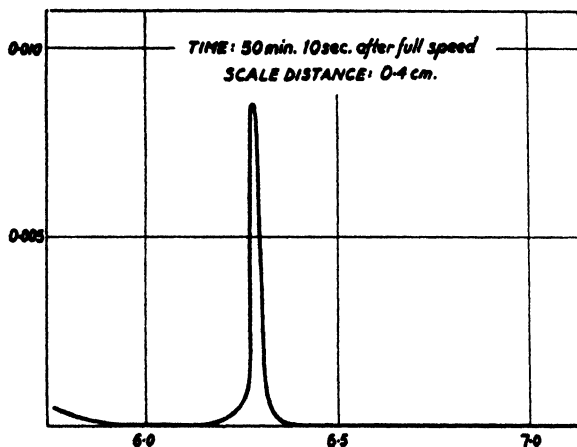


FIG. 3. Sedimentation diagram for N thyroglobulin in salt-free solution

bility region. These changes are well defined, as distinguished from the ordinary increases in polydispersity which occur on long standing in salt solutions. When sedimented, a freshly dialyzed salt-free solution of thyroglobulin less alkaline than pH 8 to 9 gives a single boundary, which moves in the cell at a slower rate due to the failure to repress the Donnan effect. In addition, the boundary possesses a considerably greater sharpness than it does in the presence of salt. In the discussions to follow we shall term this "N protein" (figure 3).

In salt-free solutions with protein concentration higher than 1.0 per cent a single well-defined slower sedimenting component, which we shall call for convenience " α -protein", is formed on standing (figure 4). An equilibrium is established, and the rate at which the change takes place is a function of the pH value of the solution. In alkaline solutions attainment of

equilibrium is rapid. At 4°C. several weeks are required for the change in solutions more acid than pH 7, but the reaction is immediate in solutions more alkaline than pH 9 to 10. The process is immediately reversed by

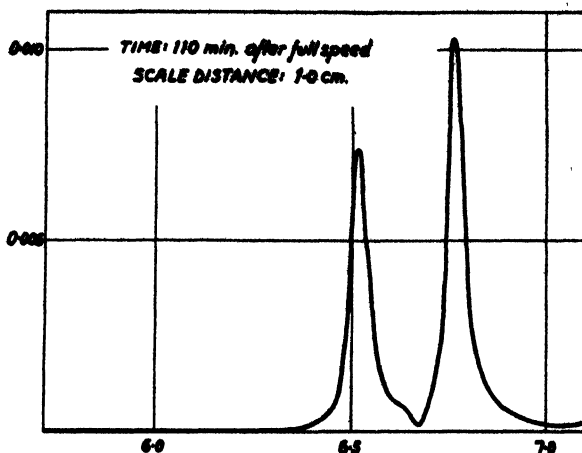


FIG. 4. Sedimentation diagram for N thyroglobulin (right) and α -thyroglobulin (left) in equilibrium in salt-free solution (protein concentration = 4.5 per cent; pH = 9.5).

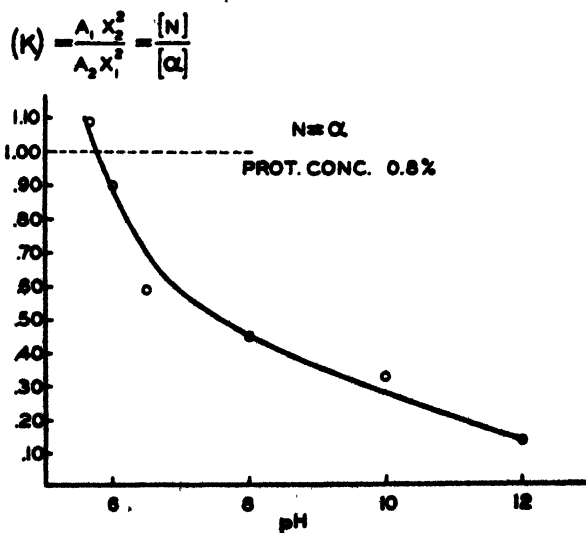


FIG. 5. Equilibrium $N \rightleftharpoons \alpha$ as a function of pH

the addition of electrolyte to 0.02 *M*, giving native protein with normal sedimentation and electrochemical behavior. At this salt concentration Donnan effects are largely repressed in routine sedimentation experiments.

Beyond pH 11.3 the equilibrium is shifted, perhaps to a reaction product from α -protein, since the process is now no longer reversible with electrolyte (figure 5).

On dilution to less than 0.1 per cent protein concentration of a solution containing the equilibrium system $N \rightleftharpoons \alpha$, a new equilibrium is rapidly established between a third slower sedimentation component (figure 6). That the newly formed, slower sedimenting protein formed in dilute solutions arises from the α -component is apparent, since freshly dialyzed dilute solutions of thyroglobulin sedimenting with a single sharp boundary do

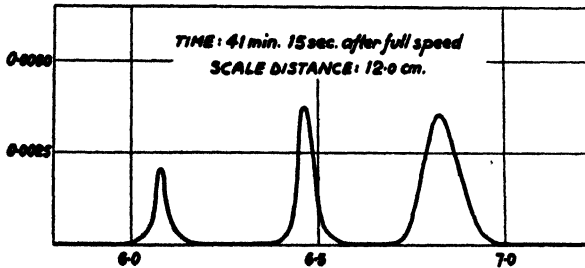


FIG. 6. Sedimentation for N thyroglobulin (right) and α -thyroglobulin (center) and slower sedimenting protein in salt-free solution (protein concentration = 0.08 per cent; pH = 9.5).

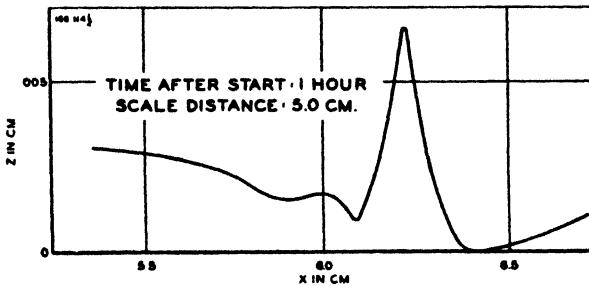


FIG. 7. Sedimentation diagram for isolated α -thyroglobulin

not appear to undergo immediate dissociation. This is further confirmed by isolation of the α -component with use of the two-compartment separation cell of Svedberg (6) (figure 7).

The separated α -form of the protein is unstable. An equilibrium is again established with time with the N protein. If the solution containing α -protein is diluted to less than 0.1 per cent protein concentration, the new slower sedimenting protein is again formed. If heated, the α -form changes to homogeneous denatured protein with sedimentation behavior like that of N protein but with different solubility and electrophoretic properties. If allowed to stand in high concentrations, especially near pH 5, components sedimenting faster than N protein have been observed.

It appears from these experiments that the α -component is an intermediate unstable form of the protein.

Equilibria of the type $N \rightleftharpoons \alpha$ are not specific to thyroglobulin, because similar reactions have been found in other protein systems. Analogous equilibria are shown for thymus nucleohistone and antitoxic diphtheria

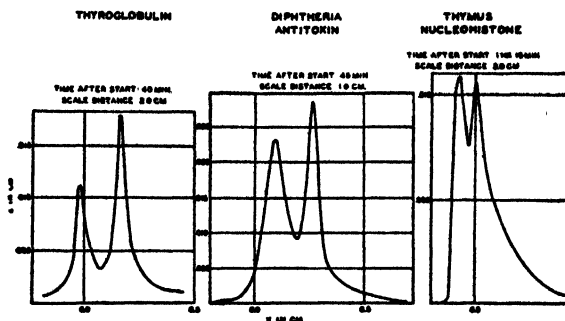


FIG. 8. Sedimentation diagram showing equilibrium $N \rightleftharpoons \alpha$ in various proteins. From left to right in each diagram, labile and native components. Concentration and pH for each protein as follows: thyroglobulin, 4.3 per cent, pH = 6.1; antitoxic diphtheria pseudoglobulin, 5.5 per cent, pH = 7.6; thymus nucleohistone, 1.2 per cent, pH = 6.0.

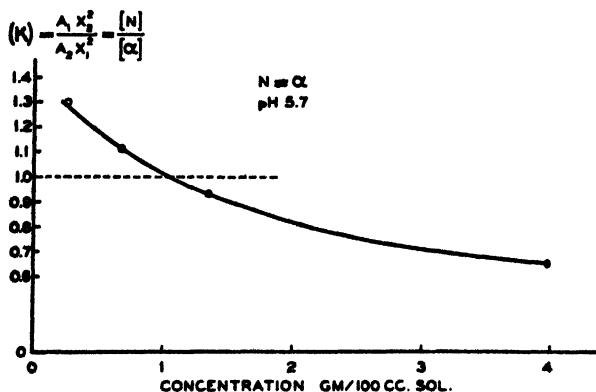


FIG. 9. Effect of protein concentration in shifting equilibrium $N \rightleftharpoons \alpha$

pseudoglobulin and are compared with the equilibrium in thyroglobulin (figure 8).

Although the system $N \rightleftharpoons \alpha$ gives a sedimentation diagram which resembles that of a dissociation, there are reasons to believe that the changes now being considered do not involve a change in mass of the kinetic unit. For instance, the equilibrium $N \rightleftharpoons \alpha$ is not shifted to the right on dilution, as would be expected on the basis of the law of mass action if the process involved an increase in the number of molecules.

Instead the equilibrium is shifted toward the N-form, as shown in the accompanying diagram (figure 9).

Such a process might be considered as a change involving an unfolding of the protein molecule in solutions. Another view would be the orientation of the rod-shaped particles in solution. However, the change is much more labile to electrolyte than the layering effects noted in concentrated solutions of tobacco mosaic virus protein ascribed by Bernal (1) as due to an orientation of the rod-shaped particles. Furthermore, it is difficult to account on this basis for the existence of equilibrium in dilute solution.

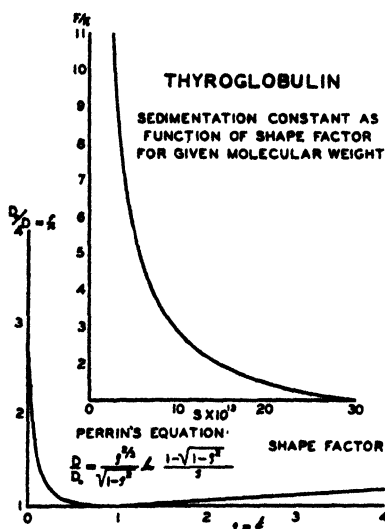


FIG. 10

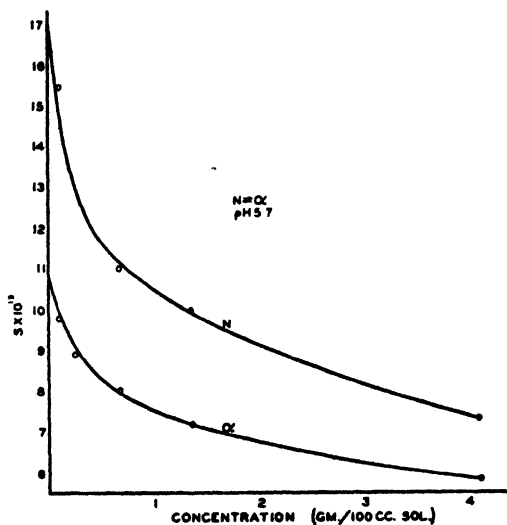


FIG. 11

FIG. 10. Upper curve: relation of dissymmetry coefficient to sedimentation constant. Lower curve: ratio of major to minor axis, b/a , through Perrin's equation and the relation between the diffusion constant for the protein and for a spherical molecule of the same molecular weight.

FIG. 11. Sedimentation rate of N and of α -thyroglobulin as a function of concentration

An unfolding of the molecule to account for the change in sedimentation behavior is indicated by the following calculation: On the basis of the dissymmetry number 1.5, given by Heidelberger and Pedersen (2) for normal thyroglobulin, it is possible to calculate the ratio of the major to the minor axis by assuming the molecule to have the shape of an ellipsoid of revolution.

The ratio b/a for normal native thyroglobulin corresponds approximately to 8.7 to 1 (figure 10). If we assume the molecule to undergo simple unfolding such that it becomes twice as long and one-half as wide, we arrive at a value, 2.63, for the dissymmetry number. This number

corresponds to a sedimentation constant of 10.9×10^{-13} for the unfolded form, as compared with 19.2×10^{-13} for normal native thyroglobulin. The actual sedimentation behavior of the N and the α -thyroglobulin as a function of concentration is shown by the accompanying diagram (figure 11). On extrapolation to zero concentration specific sedimentation constant values of approximately 10×10^{-13} and 17.8×10^{-13} are obtained. Although no attempt has been made to correct these values to the basis of a sedimentation in salt solution, it is evident that the theoretical and observed values are in reasonable agreement.

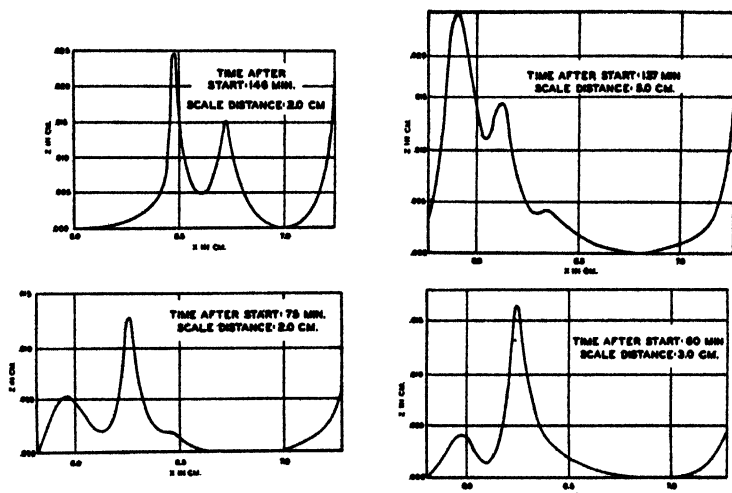


FIG. 12. Sedimentation diagram showing effect of urea on equilibrium in a single salt-free thyroglobulin solution. Upper left: equilibrium in salt-free thyroglobulin (pH = 5.5). Upper right: effect of presence of 50 per cent urea at this pH. Lower left: effect of making this solution 1 per cent in sodium chloride. Lower right: effect of addition of urea to thyroglobulin which is already in 1 per cent sodium chloride.

Although the formation of α -protein appears to involve no change in the mass, the effect of dilution in causing the formation of slower sedimenting protein from the α -form apparently does involve a change in the number of molecules and hence a dissociation. The dissociated form from α -protein is still labile to salt and is perhaps an unfolded and dissociated form of the protein.

It has been observed (3) that the presence of urea, glycine, tyrosine, and related compounds in high concentration in freshly dialyzed electrolyte-free thyroglobulin solutions favors a change in the sedimentation behavior of the protein which appears similar to that described above. These reactions can occur even in the presence of electrolytes, although in such cases higher concentrations of the addition compound are required to

produce the same magnitude of change. It would appear that in salt solutions these compounds act to overcome the effect of electrolyte in preventing the formation of α -protein. It makes no difference whether salt is added prior to the addition of urea or afterwards (figure 12). These effects appear similar to those noted by McFarlane (4) and by Pedersen (5) in other protein mixtures (*loc. cit.*).

It was shown in the section describing dissociation phenomena that, at least in certain proteins, the effect of urea or pH beyond the alkaline limits of the pH stability region in the presence of electrolyte is to cause a dissociation. With the data available it is not possible to decide whether the more complex equilibria in protein mixtures represent merely a change corresponding to α -protein or a dissociation. It is true that dissociation

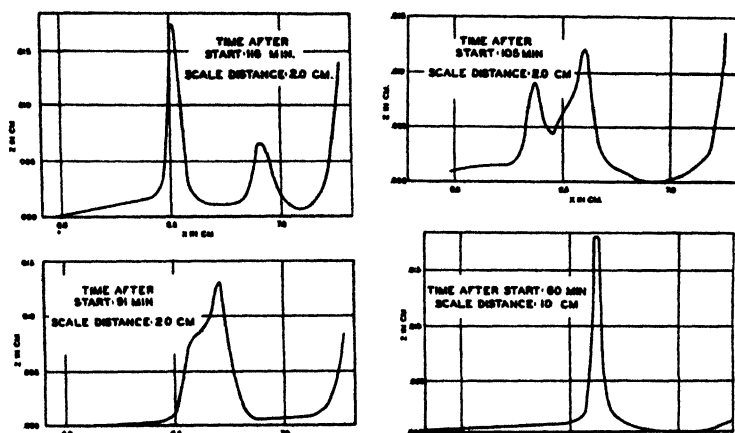
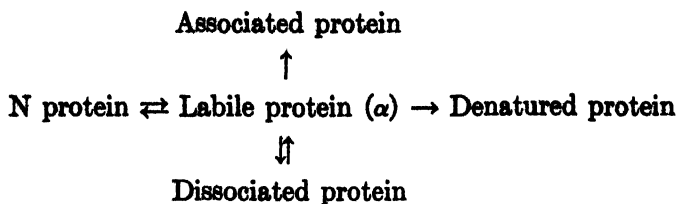


FIG. 13. Sedimentation diagram showing the effect of heat on the equilibrium in salt-free thyroglobulin solution. Upper left: equilibrium at pH 6.5. Upper right: effect of heating 10 min. at 50°C. Lower left: effect of heating 10 min. at 60°C. Lower right: effect of heating 10 min. at 95°C. to give homogeneous denatured protein.

may follow the formation of α -protein. The effect of the presence or absence of salt is very incompletely understood at the present time.

A high concentration of urea is known to favor denaturation. It would appear from this that the forces involved in dissociation and denaturation are similar. A reaction $N \rightarrow \alpha \rightarrow D$ appears involved because (1) the reaction $N \rightarrow \alpha$, in the case of thyroglobulin, is favored by heat (figure 13) and (2) further heating above 55°C. causes the α -protein to disappear with the formation, first, of an intermediate component which disappears and, finally, of a single homogeneous component which cannot be resolved from normal native thyroglobulin and which is unstable to salt to give the characteristic properties of denatured protein. It would appear that the

denatured as well as the dissociated form arose from the α -protein. These changes may be represented in the following diagram:



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REFERENCES

- (1) BERNAL, J. D.: Paper presented at the Cell Centenary Symposium, held at Stanford University, California, 1939.
- (2) HEIDELBERGER, M., AND PEDERSEN, K. O.: *J. Gen. Physiol.* **19**, 95 (1935).
- (3) LUNDGREN, H. P.: *Nature* **138**, 122 (1936); *J. Chem. Phys.* **6**, 177 (1938); *Nature* **143**, 899 (1939); and unpublished work.
- (4) MCFARLANE, A. S.: *Biochem. J.* **29**, 407 (1935).
- (5) PEDERSEN, K. O.: *Compt. rend. trav. lab. Carlsberg, Sér. chim.* **22**, 427 (1938).
- (6) SVEDBERG, T.: *Ind. Eng. Chem., Anal. Ed.* **10**, 119 (1938).

THE STRUCTURE OF THE ADSORPTION LAYER AND THE ADHESION OF MICROSCOPIC PARTICLES¹

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This paper gives a summary of the newer experiments that have been carried out by the author and his collaborators on the adhesion of microscopic particles and, in connection with this, on surface films.

First of all, it may be mentioned that some years ago a method was worked out by means of which the forces operating in coagulation may be measured directly. This method is based on allowing microscopic particles, for example, quartz particles, to settle on a plate of the same substance, and on measuring the exact force required to tear the particles off the plate. The angle of inclination of the plate at which the particles just begin to move is measured. This angle is called the angle of adhesion.

From the experiments carried out by this method, the fundamental knowledge was gained that the adhesion is caused not by gravitational force, but by the interaction of the surface films of the adsorption layers. The chemical substance of the particles and of the adhesive plate plays a rôle only so far as this is one of the factors that determine the properties of the surface films. The specific adhesion of the particles of the same size is different in different liquids, but is characteristic for the chemical structure of the adhering particles. In the same way, the specific adhesion represents a characteristic size for the chemical structure of the adhering particles.

From experiments made on different substances, it has become clear that the adhesion in different liquids is closely connected with the lyophilic properties of the substances. Table 1 gives some experimental results that have been obtained on different microscopic particles of the same size in different liquids. From these experiments it follows that an antagonism exists between the specific adhesion in dynes per square centimeter and the lyophilic character. This is especially pronounced in the cases of quartz and carbon. Quartz is very lyophilic in water, but very lyophobic in organic liquids. Accordingly, quartz shows a considerably smaller adhesion in water than in organic liquids. With carbon the case is reversed. Since

¹ Presented at the Sixteenth Colloid Symposium, held at Stanford University, California, July 6-8, 1939.

carbon is less lyophilic in water than in organic liquids, its adhesion in organic liquids is less than in water.

This procedure was used for the investigation of the structure of surface layers, since it enables us to extend our knowledge of the peculiarities arising in the adhesion of microscopic particles to plates. Adhesion studies in connection with cataphoretic measurements led directly to the question as to what conclusions may be drawn from the variations in the adhesion caused by the influence of different substances on the detailed structure of the adsorption film in solid adsorbents. For, from the statement that the

TABLE 1
Adhesion of microscopic particles in different liquids

SUBSTANCE OF THE PARTICLES	LIQUIDS	SPE- CIFIC AD- HESION	SUBSTANCE OF THE PARTICLES	LIQUIDS	SPE- CIFIC AD- HESION
		<i>dynes per sq. cm.</i>			<i>dynes per sq. cm.</i>
Quartz	Water	0.3	Pyrites	Water	2.8
	Ethyl alcohol	2.9		Ethyl alcohol	3.4
	Chloroform	3.1		Benzene	3.8
	Benzine	3.2	Coal (anthra- cite)	Water	3.8
	Benzene	3.1		Ethyl alcohol	2.4
	Toluene	3.3		Benzine	1.2
Glass	Water	0.5		Benzene	1.1
	Ethyl alcohol	3.0	Graphite	Water	3.7
	Ether	3.4		Ethyl alcohol	2.5
Barytes (BaSO ₄)	Water	4.7		Benzine	1.4
	Ethyl alcohol	5.0		Benzene	0.8
	Benzene	5.1	Gold	Water	5.8
Calcite	Water	2.8		Benzene	3.5
	Ethyl alcohol	3.4			
	Benzene	3.8			

adhesion of particles in liquids is caused by an interaction of the adsorption films, it follows necessarily that all influences that alter the structure and composition of the adsorption films are also of decisive importance for the adhesion.

As regards the alteration in the adhesion through the influence of different substances, three groups of extreme cases must be distinguished: the influence of strong electrolytes, that of weak electrolytes and non-electrolytes, and that of colloids.

The adhesion in solutions of strong electrolytes is due to the interionic (electrostatic) forces acting between the ions of the electric double layer.

The alteration in the adhesion is determined by the two characteristic variables of electrolytic systems,—the electric charge and the thickness of the electric double layer. With regard to the effect of different electrolytes on the adhesion, the following quantitative law was found to hold: In solutions of strong neutral salts, in which the activity coefficient of the effective ions has the same value, the adhesion is influenced to the same degree. The well-known activity coefficient law of Ostwald also holds good for the adhesion of microscopic particles.

In order to make a further, more detailed investigation of the correlation between adhesion and coagulation, I determined the coagulation values of different electrolytes on different suspensions—especially on monodisperse quartz suspensions—by measuring the speed of sedimentation. Parallel to these experiments, the adhesion of quartz particles on a quartz plate

TABLE 2

ELECTROLYTE	COAGULATION VALUES	ACTIVITY COEFFICIENT	ADHESION
			<i>dynes per sq. cm.</i>
NaCl	42	0.78	1.88
KCl	40	0.79	1.84
Na ₂ SO ₄	17	0.83	1.96
Na ₂ PO ₄	28	0.76	1.80
K ₂ Fe(CN) ₆	5.5	0.89	1.92
K ₄ Fe(CN) ₆	8.5	0.84	1.87
CaCl ₂	0.7	0.81	1.98
BaCl ₂	0.5	0.84	1.94
MgSO ₄	0.32	0.85	1.82
AlCl ₃	0.00012	0.96	2.05

was measured under the same conditions. The results of these experiments are given in table 2.

From these results it will be seen that, in solutions of different neutral salts, the same adhesion and the same value of the activity coefficient correspond to the coagulation value. It is true that these values are different in the case of different suspensions. This result makes it very probable that, in the case of weakly solvated disperse systems, the more important and characteristic part of the system is the dispersion medium. A disperse system is stable if the disperse particles and the dispersion medium form a harmonious unity, but this is possible only if the particles or micelles are in the same physical state as the dispersion medium, this state being conditioned by the physical structure of the adsorption film; that is to say, in a state that renders possible the building up of the particles. If this condition is not fulfilled and the structural harmony between the adsorption films and the dispersion medium is disturbed, the system coagulates, since the dispersion medium eliminates the disperse particles. According

to this theory, the active partner in the coagulation is the dispersion medium. The force of attraction among the particles plays a rôle only after the coagulation, insofar as it determines the physical properties of the coagulum.

TABLE 3
Adhesion of quartz particles to a quartz plate in alcohols

ALCOHOL	CONCENTRATION	SIN α	P
	<i>moles per liter</i>		
Methyl alcohol.....	0	0.064	17.4
	1.24	0.087	17.8
	2.48	0.105	18.3
	4.96	0.107	18.9
	7.44	0.115	20.6
	9.6	0.201	21.5
	12.4	0.309	23.5
	14.8	0.500	25.3
	17.3	0.630	27.4
	18.6	0.772	28.6
	22.3	0.920	32.8
Ethyl alcohol.....	0	0.064	17.4
	0.83	0.096	17.8
	1.66	0.101	18.3
	3.32	0.107	19.4
	4.98	0.130	20.7
	8.29	0.216	24.0
	9.96	0.743	25.5
	10.77	0.809	28.6
	11.62	0.874	29.3
	13.28	0.951	32.9
Propyl alcohol.....	0	0.064	17.4
	0.67	0.111	18.0
	1.34	0.130	28.7
	4.02	0.146	22.4
	6.70	0.500	27.3
	8.04	0.908	30.9
	9.88	0.924	35.5
	10.72	0.966	41.8

This principle proved fruitful also in the case of weak electrolytes and non-electrolytes. The adhesion in solutions of non-electrolytes is caused by the action of intermolecular forces (dipole forces, van der Waals forces) between the molecules of the adsorption films. According to this, organic compounds of different types have a different influence on the adhesion of microscopic particles. Compounds of analogous structure, for example, the members of homologous series, act qualitatively in the same way, that

is, they influence the adhesion of the microscopic particles with increasing concentration in much the same way; they show a difference only in the intensity of their effect.

The experiments with non-electrolytes,—different homologous and isomeric carbon compounds,—were of special interest in connection with the above question: namely, to what extent the structure of the adsorption layer plays a rôle in the adhesion, and also to what extent conclusions may be drawn as to the structure of the adsorption layer from alterations in the adhesion. At the same time, these experiments gave further information as to the influence of the size and shape of the molecule on the adhesion.

Among other experiments, those with the homologous series of the alcohols were very instructive. The experimental results in table 3 show the adhesion of quartz particles on a quartz plate in solutions of methyl,

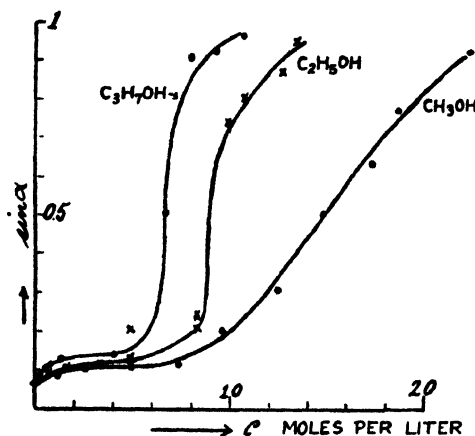


FIG. 1. The adhesion of quartz particles to a quartz plate in solutions of alcohols

ethyl, and propyl alcohols of different molecular concentrations. The experiments were carried out with monodisperse quartz powder (size of particles 14.2μ). It will be seen that $\sin \alpha$ of the angle of adhesion increases with increasing alcohol concentration and with increasing molecular weight of the alcohol. This peculiar form of the adhesion curve, figure 1, is caused by the increasing dehydration of the adsorption layers with the increasing concentration of the solution. With increasing alcohol concentration the adsorption film becomes constantly richer in alcohol molecules, and thus the intermolecular forces between the adsorbed alcohol molecules play an increasingly important rôle.

That in this case the adhesion is in fact due to the intermolecular forces between the adsorbed molecules is proved by the discovery that the adhesion bears a close relation to the dielectric molecular polarization of the

mixed liquids. The dielectric polarization of the mixed liquids, $P_{1,2}$, was calculated from the well-known formula:

$$P_{1,2} = \frac{D - 1}{D + 2} \cdot \frac{N_1 M_1 + N_2 M_2}{d}$$

in which D is the dielectric constant of the mixture and d is its density. From table 3, and especially from figure 2, it will be seen that in the case of different alcohols the same adhesion corresponds to the same P value. The $\sin \alpha$ values of the three homologous compounds lie on a common $\sin \alpha - P_{1,2}$ curve.

The above regularity was found to exist only in the case of compounds of analogous structure and chiefly in the case of homologous compounds.

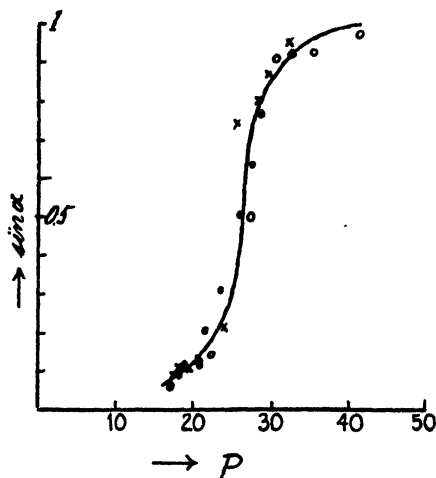


Fig. 2. The relation between adhesion and the dielectric molecular polarization for three alcohols

Compounds of different molecular structure but of the same molecular polarization have a different effect on the adhesion. This fact indicates that when alteration of the adhesion is affected by the addition of non-electrolytes, not only the dielectric properties of the liquid medium but also other properties, especially the molecular constitution and the size and shape of the dissolved molecules, are of great importance.

Besides the properties of the dissolved portion, those of the solid phase are also important. In this respect also the electrical properties proved to be the most decisive factors. This is especially pronounced in the case of solutions of polar and asymmetrical compounds, for instance, in those of the aliphatic acids. Experiments carried out with quartz showed especially clearly to what a great extent the original nature of the electric charge influences the whole character of the concentration curve of the

adhesion. Figure 3 shows the effect of water-soluble aliphatic acids on the adhesion of quartz particles with a negative charge to a negatively charged quartz surface.

In the case of low concentrations we are dealing essentially with an electric action, a discharge. With high concentrations strong dehydration takes place; accordingly in this case also the adhesion shows a considerable increase, as in the case of the alcohols. On the other hand, we find quite different conditions in the case of positively charged quartz. The quartz particles and the adhesive plate were given a positive charge by means of an aluminum salt, and the adhesion was measured under the same conditions as those of the negatively charged quartz. The results are shown in figure 4.

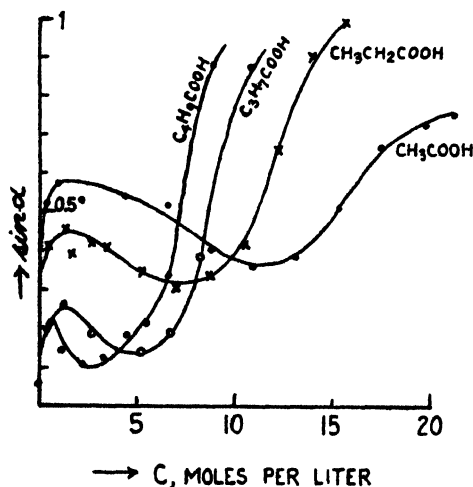


FIG. 3. The adhesion of quartz particles with a negative charge to a negatively charged quartz surface in solutions of aliphatic acids

Three concentration zones can be distinguished. With low concentrations we have a simple ion action. This is shown by the speed of the cataphoretic motion on the lower curve. Parallel to the recharging, first a decrease and then an increase in the adhesion take place. The minimum adhesion coincides with the maximum of the negative electrokinetic potential. At higher concentrations, however, the change of the electrokinetic potential has a noticeable influence on the adhesion; for with higher concentrations, the adhesion is independent of the concentration, although the electrokinetic potential decreases further with increasing concentration.

From the first it seemed a probable hypothesis that these phenomena might have their origin in an alteration of the dipole double layer formed on the quartz surface by the orientation of the aliphatic acid molecules. To a great extent the abovementioned experimental results seem to in-

indicate the following change in the adsorption layer: First of all, a monomolecular film is formed, in which the molecules of the carboxyl group ad-

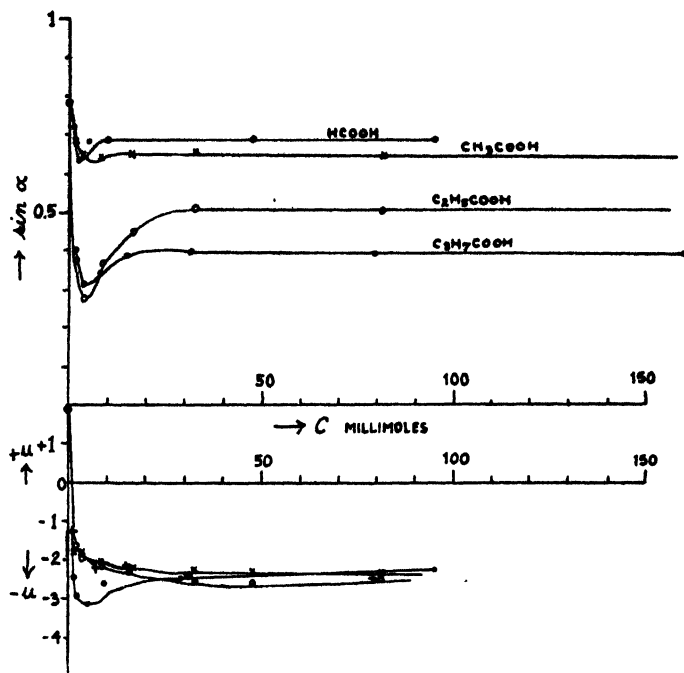


FIG. 4. The adhesion and the cataphoretic mobility of quartz particles with a positive charge in solutions of aliphatic acids

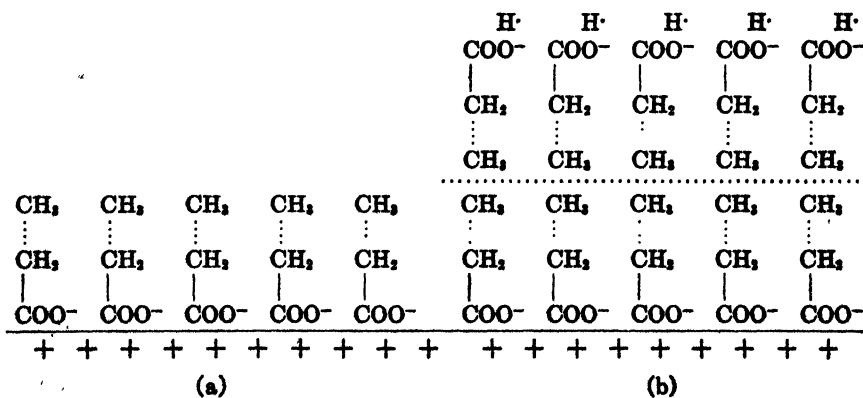


FIG. 5. Orientation of aliphatic acid molecules on the quartz surface

here to the positive quartz surface. Condition a (figure 5) corresponds to the isoelectric point. Later a second layer, b, is deposited, in which the carboxyl groups occupy the outer position. The second layer gives the

surface a negative charge, the value of which is determined by the dissociation of the carboxyl group. The thickness of this bimolecular layer chiefly determines the adhesion, as is evidenced by the fact that the adhesion is independent of the concentration in more concentrated solutions.

The most decisive experiments in this connection, however, were those made on the molecular films of stearic and palmitic acids. Following the method of Langmuir and Blodgett, films built up alternately of stearic and palmitic acids were produced on a quartz plate positively charged with aluminum ions, and on this plate the adhesion of quartz particles, also positively charged, was measured in water. The results are shown in figure 6.

On the monomolecular film the value of the angle of adhesion is 22° . If the plate is once more dipped in water and drawn through the surface

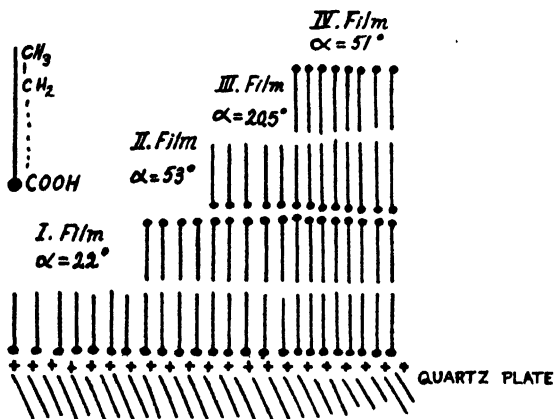


FIG. 6. Films of stearic and palmitic acids on a quartz plate positively charged with aluminum ions

film of stearic acid, a second film is built up on the plate, in which the COOH groups are on the outside. On this second film, the angle of adhesion is 53° . If a third film is built up, the adhesion again decreases, and the angle of adhesion shows a value of 20.5° ; on the fourth film, the angle of adhesion again shows the same value as on the second film. That is, on these alternate films the adhesion changes alternately. So these experiments show clearly that, as regards the change in the adhesion in solution of polar compounds, the orientation of the adsorbed dipoles plays a decisive rôle.

It should be mentioned here that such alternate films exhibit a periodic change in their activity in the case of heterogeneous catalysis. Quartz plates were covered with polymolecular stearic acid films, and the rate of decomposition of hydrogen peroxide was measured in the presence of these plates. As the numerical values in table 4 show, the rate of decomposition

varies according to whether the alkyl or carboxyl group is on the outside in the outermost film.

As would be expected, these investigations led to the problems of the high-molecular compounds, first of all to those of the albumins. The albumins also have a very characteristic influence on the adhesion, but the

TABLE 4

The catalytic activity of polymolecular stearic acid films (adhering to quartz) on the decomposition of hydrogen peroxide

Original concentration of the solution of hydrogen peroxide, 0.1 mole per liter;
volume of the solution, 100 cc.; five quartz plates, with a surface of about
40 cm.² each

	QUANTITY OF H_2O_2 DECOMPOSED WITHIN 24 HR.
	moles per liter
Without quartz plates.. . . .	0.0004
In the presence of plates covered with a single film	0.0069
In the presence of plates covered with a twofold film	0.0134
In the presence of plates covered with a threefold film.	0.0056
In the presence of plates covered with a fourfold film.	0.0138

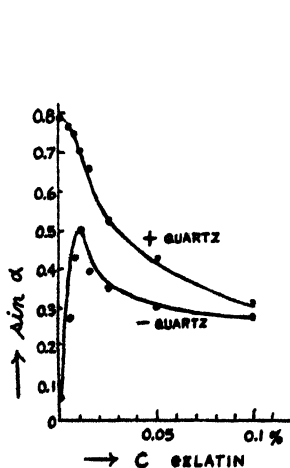


FIG. 7

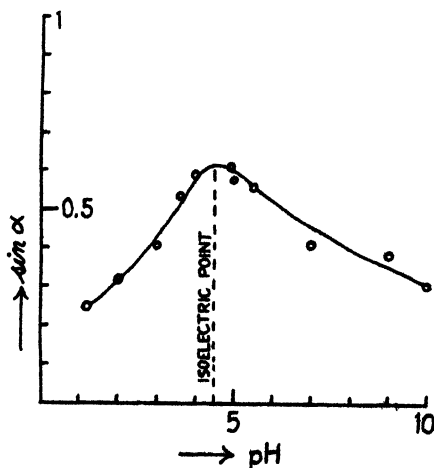


FIG. 8

FIG. 7. The effect of gelatin on the adhesion of quartz particles

FIG. 8. The adhesion of quartz particles in gelatin solutions of different pH values

conditions in the case of the albumins are more complicated, since here an interaction of the adsorption films of the adsorbed colloid must be taken into account. Nevertheless, in this field also several regularities have been detected.

In the first place it was found that the different albumins have a very

individual effect on the adhesion of microscopic particles, especially on quartz particles. In addition to the individual properties and the physical condition of the albumins, the electric condition of the quartz surface is of great importance. This is clearly shown, among other things, by the concentration functions of the adhesion. These functions yield us information principally with regard to the sensitizing and protective action of the colloids. In figure 7 the upper curve refers to positively charged quartz particles. With increasing concentration the adhesion shows a

TABLE 5

Connection between the building up of collagen fibers and the adhesion in solutions of electrolytes

ELECTROLYTE	CONCENTRATION OF ELECTROLYTE	THE ADHESION (SIN α) OF QUARTZ PARTICLES IN COLLAGEN SOLUTIONS	BUILDING UP OF FIBERS
	<i>moles per liter</i>		
Sodium chloride . . .	0	0.27	
	0.005	0.31	
	0.01	0.32	
	0.05	0.46	Faint
	0.10	0.59	Very noticeable
	0.15	0.64	Strong
	0.20	0.66	Faint
	0.30	0.72	
	0.40	0.73	
Barium chloride....	0	0.27	
	0.0001	0.32	
	0.0002	0.34	
	0.0005	0.38	
	0.001	0.44	+ charge
	0.002	0.53	Faint
	0.005	0.58	Strong
	0.007	0.64	Strong
	0.01	0.72	Faint
	0.02	0.58	Very faint
	0.03	0.46	
	0.04	0.42	
		isoelectric point	
		- charge	
			Faint
			Strong

steady decrease; this signifies a protective effect. On the other hand, the lower curve, which has been obtained on negatively charged quartz, shows first a sensitizing effect, the protective action manifesting itself only with higher concentrations.

It is true that the shape of these concentration functions depends on the physical state of the albumin. The electrical condition is especially important. This is evidenced by the fact that the adhesion exhibits a maximum at the isoelectric point of the albumin. This is shown, for example, by the adhesion of quartz particles in gelatin and in albumin

solutions of different pH values. The isoelectric point is especially sharply defined in both cases (figure 8). This method is therefore very suitable for the determination of the isoelectric point of colloids.

The circumstance that the adhesion of solid particles in solutions of albumins is due principally to the interaction of the adsorbed micelles led to the problem of the structure of the biogels. One of several important questions is: What circumstances determine the building up of fibers and fibrous gels out of the submicroscopic particles? A concrete case, for example, is that of the collagen fibers. It is generally known that by the action of electrolytes under certain circumstances fibrous gel is built up out of diluted collagen solutions which may be obtained from rats' tails by means of acetic acid. To detect the conditions under which collagen fibers are built up, various electrolyte solutions of different concentrations were added to the collagen solution and observations were made by means of a microscope as to the concentration at which the building up of the fibers takes place. Parallel with these observations, the adhesion of quartz particles in these solutions was determined under the same conditions, and their cataphoretic mobility was also measured. These experiments (table 5) showed that the fibers never form at the isoelectric point, that is, never at the maximum of the adhesion. The building up of the fibers takes place only near the isoelectric point, that is, in the state of the solution in which the attractive forces between the micelles are not great enough to prevent their orientation during coagulation. This effect is seen very clearly in the case of barium chloride solutions, where the sign of the electric charge on the micelles is reversed. As may be seen, the building up of fibers takes place both to the left and to the right of the isoelectric point, but not at the isoelectric point itself (table 5). From such observation of the behavior of adsorbed albumin films on adhesion it is believed that further information may be obtained concerning the nature and properties of the biogels.

It is hoped that this summary gives a satisfactory survey of the phenomenon of adhesion and that it serves to indicate the fruitfulness of this field for biology and technics.

In conclusion the author wishes to express his great appreciation of the invitation to give a paper before the Colloid Symposium and of the opportunity thus afforded to make the acquaintance of his American colleagues.

THE BEHAVIOR OF COLLOIDAL SUSPENSIONS WITH ELECTROLYTES^{1, 2}

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INTRODUCTION

When, in 1861, Quincke (46) presented his data showing that, in general, substances of a colloidal nature possessed an electrical charge when in contact with a liquid, he formulated the idea of a double layer of charge, each layer opposite in sign, existing at the interface. Both of these he considered to be held rigidly in place, one layer of charge held at the surface of the substance and the other restrained in the liquid medium.

Later this idea formed the basis of the Helmholtz (25) double layer theory and, finally, the Gouy (17) diffuse double layer theory, both of which attempted to explain the electrodynamic, stability, gelation, and coagulation characteristics of colloidal systems. Today the Gouy theory, with slight modifications, is still most generally accepted by colloid chemists as offering an adequate picture of the properties of electrocratic colloids in dispersion.

To account for the existence and the formation of the electrical double layer at colloidal surfaces, two theories have been proposed. The adsorption theory, favored by Krut (27), Rabinowich (48), Weiser (56), and their coworkers and others, postulates that the ionic layer which confers the fundamental charge on a colloidal particle is firmly held at the surface by means of the preferential adsorption of ions from the dispersion medium, whereupon the ions of opposite sign form a diffuse system about the particle, owing to electrostatic attraction.³ The solubility or ionogenic complex theory, whose main exponents are Duclaux (10), Nicolardot (39),

¹ Presented at the Sixteenth Colloid Symposium, held at Stanford University, California, July 6-8, 1939.

² This paper is largely based on experimental work undertaken by S. Hirshon and compiled in his Master of Science thesis, Massachusetts Institute of Technology, 1939.

³ For a critical discussion of the ideas favoring the adsorption theory see H. B. Weiser (Inorganic Colloid Chemistry, Vol. II, p. 76, John Wiley and Sons, Inc., New York (1938); and Vol. III, pp. 118 and 220, John Wiley and Sons, Inc., New York (1939)).

Pauli (42), Valko (43), and their coworkers, attributes the formation of the diffuse layer to ions dissociated from the colloidal particles, which themselves are considered as complex colloidal salts. The charge on the particles exists because of the free valence ions on the surface of the complex salt. It must be admitted that the experimental evidence is by far in favor of the adsorption theory.⁴ The ionogenic complex theory finds serious difficulty in explaining such simple experiments as those performed by McTaggart (35), showing the existence of an adsorbed charge on air bubbles.

Modern theories attempt to go one step further in regard to these ideas. Having obtained, in general, a picture of the colloidal micelle which comprises the nucleus, of its surrounding ions, and of the process by which it is formed, they attempt to explain the interaction of the colloidal micelles with one another to produce coagulated, gelled, or stable systems.

Freundlich (12), Hamaker (19), Houwink (26), and Kallman and Miss Willstätter (27) have analyzed colloidal suspensions, considering that the behavior of the individual particles in lyophobic (electrocratic) sols is controlled mainly by long-range van der Waals attraction forces and electrical repulsion forces, acting over shorter distances and due to the interaction of the diffuse ionic layers. On the basis of these assumptions, potential energy curves have been drawn representing the summation of the repulsion and the attraction forces as a function of the distance separating any two particles. A colloidal suspension is considered stable when the net repulsion force acting between the particles is considerably greater than their kinetic energy, the force impelling the particles together. The system may be considered gelled when the particles lie at suitable distances from one another in minimum potential energy troughs formed under proper concentrations of electrolyte or concentrations of the sol, where a finite force will be required to move them. Finally, the system may be considered to be unstable when the net repulsion force between the particles has a value that is less than the kT of the particles.

The theory appears to explain the behavior of colloidal suspensions in general, but the assumption of long-range van der Waals forces, which is necessary to account for the behavior of fairly dilute sols, has not to our knowledge been verified by experimental evidence. On the contrary, Langmuir (30) has demonstrated with work on monolayers that the so-called molecular forces that are exerted between particles are usually effective only up to the distance of one molecular diameter. This was deduced from data which showed that, in general, on a given surface only the first molecular layer was held by surface forces, and also that changes

⁴ Admittedly the solubility theory may find application in the case of colloidal dispersions of high molecular weight, e.g., proteins, soaps, etc., which are known to ionize in solution.

in the contact angles of liquids resting on a surface covered with a monomolecular layer could be ascribed to inversion of the molecules in the layer rather than to long-range forces. Langmuir has also pointed out recently that the theory fails to take into account the attraction forces due to the counter ions in the dispersion medium, which are sufficient to account for the cohesion of the particles in coagulation (30). The theory also fails to take into direct account thermal agitation and the variability of micellar charge on the individual particles which, in general, depends upon the concentration of micelles.

Houwink (26) states that at present it seems impossible to explain, on the basis of the potential trough idea, the decrease in yield point that occurs with an increasing viscosity upon the addition of sodium chloride to a concentrated clay slip, although the theory from a physical viewpoint can explain the formation of gels in these systems.

Thus at present the assumption of long-range van der Waals forces does not appear to be verified by experimental evidence nor does it appear to have a general application in explaining completely the physical behavior of any given colloidal system.

Ostwald (40, 41) considers the coagulating forces of a sol to be the same as the interionic attraction forces in the dispersion medium. The activity coefficient of the counter ions in solution is thought of as a measure of these forces and is defined in accordance with the Debye-Hückel theory (6) by the relation

$$\log f = -0.5(Z)\sqrt{u}$$

in which Z is the valence of the counter ion and u is the ionic strength.

$$u = 0.5 (M_1Z_1 + M_2Z_2)$$

where M_1 is the molality and Z_1 the valence of the anion, and M_2 is the molality and Z_2 the valence of the cation. Ostwald pictures a lyophobic hydrosol as resembling a mixed crystal, in that it consists of comparatively large micelles built into a highly disperse ionic lattice. With the aid of considerable data he has attempted to show that, for an arsenic trisulfide sol, coagulation takes place at the same activity coefficient value of any precipitating, or counter, ion. Fair agreement is shown by the coefficient values expected from the theory and those obtained from the data. However, the theory is admittedly applicable only to the effect of neutral salts on lyophobic sols. Correlation appears to be obtained by the increase in the activity coefficients of mixtures of salts and their effect on ion antagonism. Figure 1, taken from Ostwald (41), is an example of theoretical calculations showing that antagonism becomes more pronounced, the larger the valence difference between two salts, as in the combination of a monovalent salt with polyvalent salts.

Although Weiser (58) points out that considerable variations (up to 100 per cent) in the data were ironed out by the method of averaging values to obtain agreement between theory and experiment, the idea appears to have some basis, at least qualitatively. It is important to notice that the ions in the dispersion medium play an important part in the phenomenon of coagulation; this is a point of great significance.

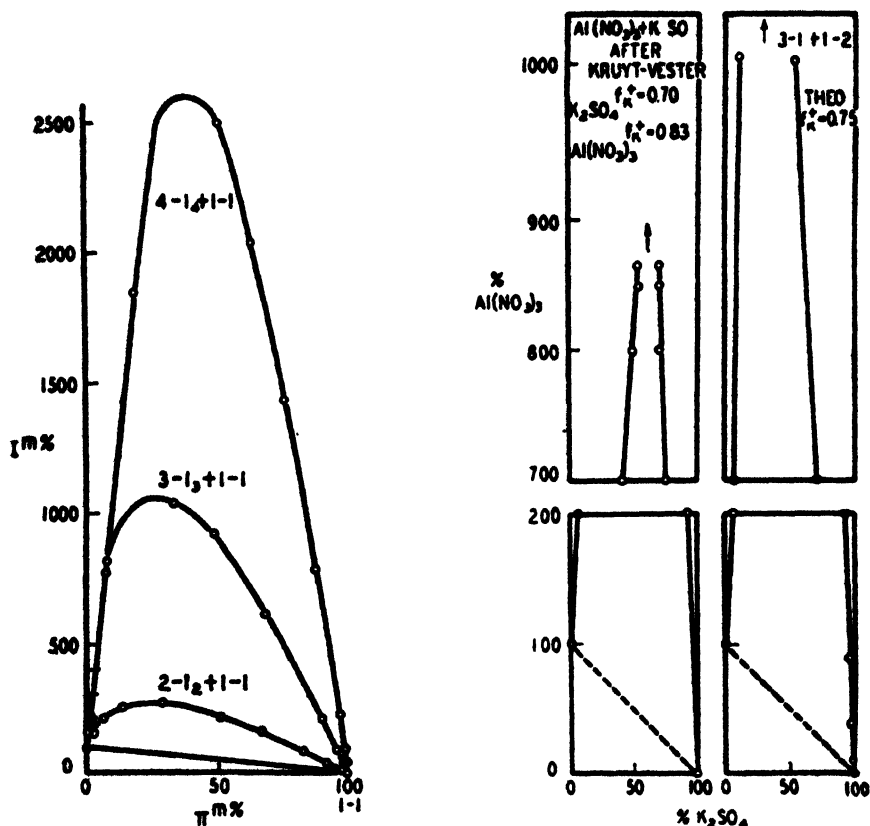


FIG. 1. (a) Coagulation by a monovalent salt combined with a polyvalent one. (b) An example of the attempt to evaluate experimental cases quantitatively by Ostwald's theory (taken from Ostwald).

Recently Langmuir (29) and Levine (31) have attempted, applying theoretical considerations, to explain the electrolytic behavior of colloidal systems solely on the basis of the interaction of the ions in the system, by using modifications of the Debye-Hückel (6) theory. Langmuir believes that the coagulation of a sol can be considered as the shrinking of an "energy lattice," where the attraction forces are mainly between the colloidal particles and the charge of the counter ions in solution possessing

an opposite sign. To account for the stability, coacervation, and the gelation characteristics of a colloidal system, he requires some new repulsive force to balance the excess or electrostatic attraction and proposes an osmotic pressure term based on $p = nRT/V$, where the symbols have their usual significance. To allow for a decrease in the Coulomb attraction forces he postulates that a definite zeta potential, rather than a definite charge, should be assumed on the colloidal particles. This last assumption is contrary to the general behavior of colloidal systems, which at different stages of electrolytic purity show varying zeta potential values as calculated from the Helmholtz-Gouy equation.

Levine differs from Langmuir, in that he construes the repulsive forces as originating from the charges on the particles in the system, which operate at short distances of separation of the particles. The attraction force he considers as arising from the Coulomb forces of attraction between the charges on the particles and their overlapping ionospheres, which are opposite in sign. He neglects the effect of the repulsion forces existing between the ions of like sign in the overlapping ionospheres, although this appears to be as important as the attraction forces between ions of opposite sign, and considers that overlapping may occur without deformation. Also, one must deduce from both Levine's and Langmuir's concepts of the electrolytic interaction of two colloidal particles that overlapping of the ionospheres must always occur, since otherwise two particles which have the same net charge must always repel each other when separated, owing to the electrical forces. However, the continual overlapping of ionospheres remains to be proven.

Furthermore, since both Langmuir's and Levine's theories are based on the Debye-Hückel theory of electrolytes, one must accept with reservations the formulas that they use representing the condition of the electrical forces between any two particles of colloidal dimensions. Hartley (20) (see also Mukherjee (38)) has pointed out that the ionic strength principle and the Boltzmann equation upon which the Debye-Hückel theory is based break down with ions of higher valence and with ionic concentrations that are not extremely dilute. In general, the concentration of ions in colloidal systems where gelation and coagulation phenomena take place is relatively high.

Notwithstanding that these authors admittedly fail to show adequate experimental data supporting their theories, and that the theoretical ideas upon which they are based have inherent defects, these ideas are a step forward in the direction advocated by Hartley (20), who pointed out that "in order to account for experimental results, some kind of association between the micelles and the ions of opposite sign must occur" and that "the effect of this on the properties of the solution may be numerically greater than the direct atmosphere effects, but it will be considerably modi-

fied by them." It may be seen also that these ideas are related to those of Ostwald (41), in that the interionic forces of the dispersion medium have assumed a greater significance in stability, gelation, and coagulation of colloids.

Thus it is evident that the realization of the importance of the "counter ions" in a colloidal suspension in controlling the behavior of the system has resulted in a new trend of ideas in order to take this effect into account.

It is our purpose to discuss below a new theory, which was derived independently from an analysis of the viscosity behavior of mixtures of iron oxide and bentonite sols. It differs from the ideas above in that (1) it presents a concrete picture of the arrangement and distribution of ions in gelation and coagulation, and (2) it considers that the ions in the dispersion medium apart from the micelles may interact with the colloidal micelles and produce gelled or coagulated systems.⁵

THE MUTUAL REACTION OF SOLS

Although considerable data have been obtained on the mutual neutralization of two sols, the order of their precipitation power, and their behavior

⁵ In opposition to theories which attempt to explain the anomalous behavior of colloidal suspensions on the basis of repulsive and attractive forces where otherwise the particles are independent of one another, Goodeve (16) considers that anomalous viscosity behavior occurs in colloidal suspensions where the particles are rod-like in shape and interfere with each other mechanically. For example, he assumes that the gelation of a bentonite suspension is due to the formation of links between the individual particles. When the system is disturbed by shearing forces, the rate of breakdown of the links between the particles caused by impulses along the linked chains determines the apparent viscosity of the system. However, Hauser and leBeau (21) present convincing ultramicroscopical evidence on a carefully fractionated system of bentonite, showing that when it is gelled the individual particles are separated from one another and that the formation of ultra flocks is an indication of the first stage of coagulation. Furthermore, small particle fractions of bentonite show little twinkling in the ultramicroscope, indicating that the degree of anisometry is not excessive. This is in agreement with the results obtained by Langmuir (29) on fractionated bentonite by polarimetric methods of analysis. He found that the ratio of length to breadth of the bentonite particles probably did not exceed the ratio of about 10 to 1, and that the particles are plate-like in shape. This evidence is supported by the work of other investigators (32). Thus it appears that the assumptions upon which the mechanical theory of gelation are based—namely, that the particles form a continuous scaffolding structure and that they are generally of rod-like shape, which would be necessary to account for structure formation in dilute systems—do not appear to be verified.

Admittedly, however, in concentrated colloidal suspensions, mechanical and hydrodynamic effects may be of some importance in determining the viscosity behavior of the system, but hydrodynamic theories (see reference 49) are found to predict the viscosity effects of a suspension sometimes 100 times less than found by actual experiment. It would appear, then, that these ideas do not concern themselves with the predominating influences controlling the viscosity behavior and gelling characteristics of colloidal systems in general.

with various concentrations of electrolytes (24), it has been only comparatively recently that the formation of thixotropic gels consisting of a mixture of two suitable sols opposite in sign (22) was reported. Apparently, then, suitable mixtures of two sols of opposite sign can be made to react, in the same manner as pure sols with electrolytes, since gelation or coagulation can be produced with them. In spite of this similarity, the viscosity characteristics and the gel-forming behavior of such systems have been investigated by few and limited experiments. For the purpose of investigating the viscosity behavior of mixtures of sols of opposite sign, two systems consisting of iron oxide and bentonite were selected which, when mixed in suitable quantities, exhibited the phenomena of gelation and coagulation to a high degree. Each sol when mixed with appropriate amounts of electrolyte formed thixotropic (50) systems. Since the rotating-cylinder type of viscosimeter was shown by Pryce-Jones (45), McMillen (34), and others to be well adapted to yielding significant results in systems that are anomalous in their viscosity behavior, it was used in studying these mixtures.

EXPERIMENTAL PROCEDURE

Various samples containing different percentages of a mixture of carefully fractionated and dialyzed iron oxide and bentonite sols were prepared. The samples were maintained at a constant temperature prior to and during the time their viscosity behavior was determined. The Mac-Michael viscosimeter was employed to determine their behavior at a constant rate of shear as a function of time. Since thixotropic gels are known to behave differently depending upon their previous mechanical history, all samples, except for special reasons, were stirred by a constant high-speed stirrer for a constant length of time prior to measurement of viscosity. The same sample was employed for a series of runs after having been aged for three weeks before use.⁶

The stock solutions consisted of a dispersion of Wyoming bentonite of 1.83 per cent concentration, having a pH of 2.28 and a sorption capacity of 94 (milliequivalents per 100 g. of clay), and Merck's 5 per cent "ferrum oxydatum dialysatum purum," which was redialyzed prior to use and had a pH of 3.45.

THE RESULTS AND THEIR INTERPRETATION

The most significant results of the experimental work as outlined above are shown graphically on the following pages. They refer mainly to the viscosity behavior of iron oxide-bentonite systems, as determined by a viscosimeter of the rotating type.

⁶ The detailed experimental data are assembled in the Master of Science thesis of S. Hirshon, Massachusetts Institute of Technology, 1939.

Figure 2 demonstrates that when the iron oxide sol is added to the bentonite sol the final equilibrium viscosity of the system goes through a first maximum and decreases through a minimum, whence it goes through a second maximum. The minimum region is evidently a coagulation effect, as was shown by the appearance of large agglomerates in the viscosimeter and by the low viscosity and absence of yield point of these systems. The first maximum may be considered as the greatest gelation effect induced in the bentonite sol by the addition of the iron oxide particles, and the second maximum as the greatest gelation effect in the iron oxide sol as induced by the addition of the bentonite particles.

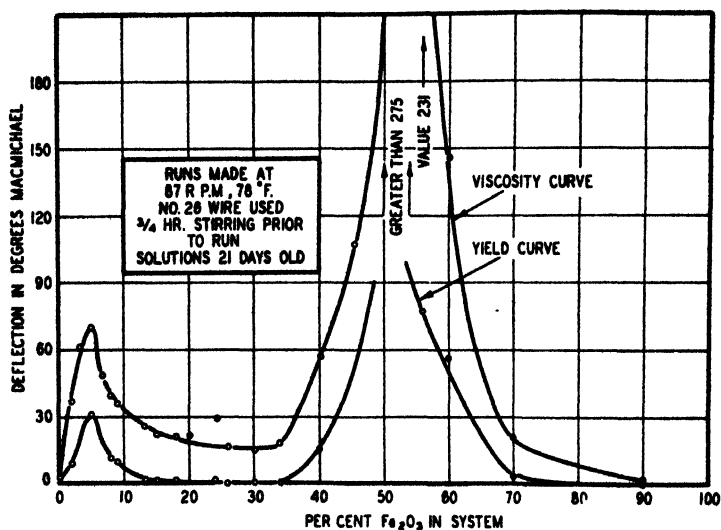


FIG. 2. Final equilibrium viscosity of various iron oxide-bentonite mixtures obtained with a modified MacMichael viscosimeter.

In the region of the curve included between the viscosity of the pure bentonite system and the center of the coagulated region, the systems were seen to undergo a pronounced change to a lighter color as they were stirred in the viscosimeter. This was taken as evidence that the bentonite particles were agglomerating about the iron oxide particles in this region as the system was brought into equilibrium. On the remaining portions of the curve the systems became slightly darker in color as they were brought into equilibrium. This indicates that in this region the iron oxide particles were agglomerating about the bentonite particles. (These effects may be independently observed by adding a small drop of an iron oxide sol to a considerably larger quantity of bentonite sol; the large flocks which form may be seen to consist of an inner nucleus of dark iron oxide

particles surrounded by the lighter colored bentonite particles. The reverse can be demonstrated by using an excess of iron oxide sol.)

This seems to show that as the iron oxide sol is added to the bentonite sol, the bentonite particles orient about the iron oxide particles, the greatest extent of this type of orientation occurring at the maximum point in the first region. *Orientation* is considered to occur when the forces acting in the system are sufficiently great to cause the particles to arrange themselves in minimum energy positions with respect to each other and the ions surrounding them. Then, finally, the bentonite particles begin to act as nuclei for the iron oxide particles to orient and to condense around them, and the maximum effect of this behavior appears to occur at the second

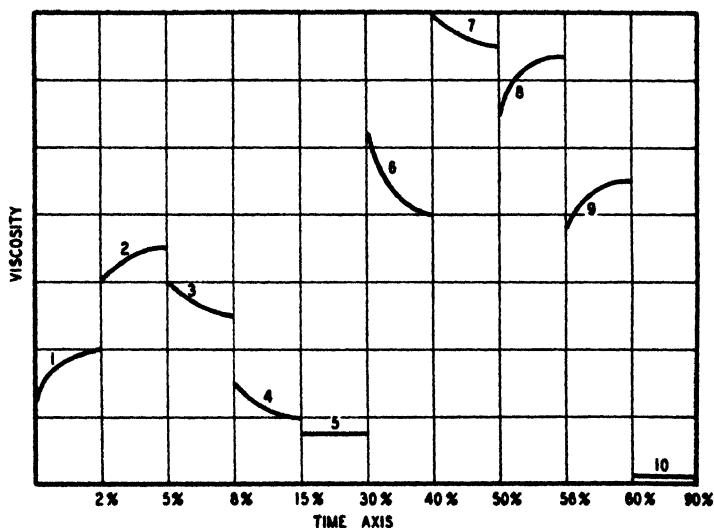


FIG. 3. Viscosity curve trends of various iron oxide-bentonite mixtures obtained from original curves. Per cent of Fe_2O_3 is given at right-hand edge of curves.

maximum. *Condensation* is considered to occur when the system contracts as a whole (syneresis) or tends to form flocks.

These orientation and condensation effects are borne out by the trends of the viscosity curves of the various systems whose viscosity behavior was determined independently. Figure 3 shows that, up to the maximum in the first region of the curve (figure 2), the viscosity of the systems increases from a low value to a high value as the equilibrium condition is reached. This is no doubt due to the increased orientation of the bentonite particles about the iron oxide particles as the shearing of the system continues. After the first maximum, the trends of the curves show that the viscosity of the systems drops from a high value to a low value as they reach equi-

librium conditions (curves 3, 4). This behavior demonstrates that, as a result of incipient coagulation, the particles are condensing closer to each other as the shearing forces continue. At this stage individual flocks, which are less dependent upon one another, tend to appear. The action of the stirrer previous to the viscosity measurement had partially deflocculated the system. The maximum coagulating effect is shown by curve 5, which is a straight line, indicating that the viscosity of the system was constant throughout the time of measurement. Thus the viscosity effect in this system was due mainly to the mechanical interference of the coagulated flocks.

As is seen from the trends of the remaining viscosity curves, the effect of the addition of bentonite sol to one of iron oxide yields effects in the initial stages similar to those obtained in the addition of iron oxide to bentonite. Thus curve 9 shows that the viscosity of the system increases

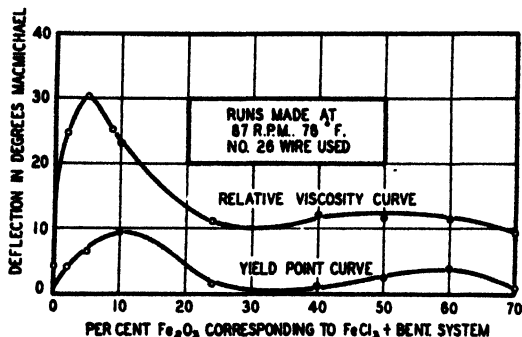


FIG. 4. Final equilibrium viscosity of various bentonite-iron chloride mixtures obtained with a modified MacMichael viscosimeter.

from a low value to a high value as the equilibrium point is reached, demonstrating the effect of the orientation of the iron oxide particles about the bentonite particles.

The curves shown in figures 5 and 6 represent the viscosity behavior of the bentonite plus iron chloride mixtures, where the amount of iron chloride added to the bentonite system corresponded to the amounts of iron chloride found by analysis as impurity in the bentonite-iron oxide mixtures.

As shown by figure 4, the viscosity trends of these systems are in their first stages the same as in the iron oxide-bentonite mixtures.

What is still more important is that the viscosity behavior of the individual curves, as shown in figures 5 and 6, approximates the same behavior as exhibited in either the first or second region of the iron oxide-bentonite mixtures (figure 3). This would appear to indicate that the general mechanisms controlling the viscosity behavior of the iron oxide-bentonite mixtures were the same as in the bentonite-iron chloride suspensions.

Thus again we may interpret these curves on the basis of orientation and condensation effects, but it is evident that in this case these must concern themselves with the reaction of the bentonite particles with the ions in the solution. Such an analysis leads us to the following concept:

Since in the iron oxide-bentonite mixtures the bentonite particles were initially considered to be orienting and later condensing about the oppositely charged iron oxide particles, we may consider that here the bentonite

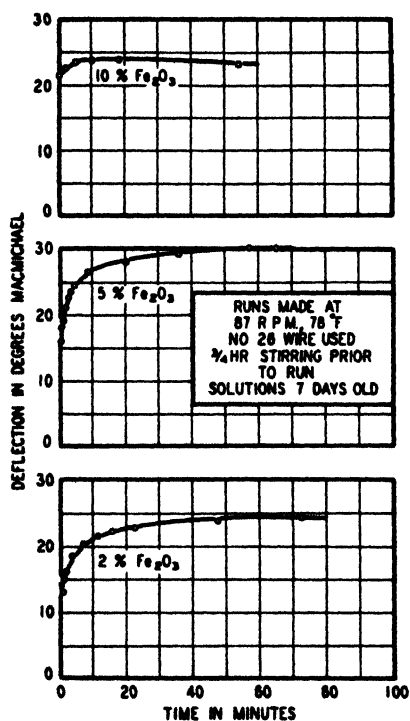


FIG. 5

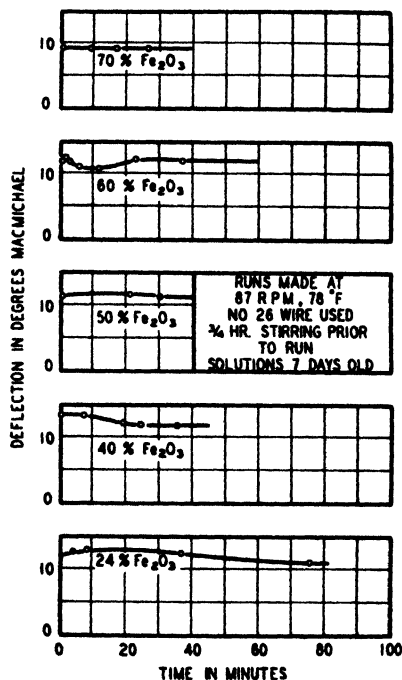


FIG. 6

FIG. 5. Original viscosity curves of bentonite-iron chloride systems, showing their behavior under constant rate of shear as a function of time.

FIG. 6. Original viscosity curves of bentonite-iron chloride systems, showing their behavior under constant rate of shear as a function of time.

particles are orienting and condensing about the ions of opposite charge in the dispersion medium. This may be considered to occur probably by adsorption of the chloride ions on to the bentonite particles, thus increasing their charge and the orientation of the now highly charged particles about the oppositely charged H^+ and Fe^{+++} ions in the dispersion medium. If this is true, then we must consider a new picture for the arrangement of ions in a colloidal system where a great amount of preferential adsorption is exhibited by the colloidal particles present.

We know that the electrical forces associated with a given colloidal particle in electrolytic media arise from two sources. One set of forces arises from the ions predominantly of one sign, which are rigidly adsorbed on the surface of the particle, and the other set arises from the ions of opposite sign, which gather about the particle in an effort to neutralize this charge. Since the particle possesses a net charge, we may assume that the total number of ions that gather about the particle in accord with the Gouy concept are not sufficient to neutralize the charge on the particle. Some of these ions of opposite sign may be floating about in random motion in the dispersion medium so that the dispersion medium has a charge

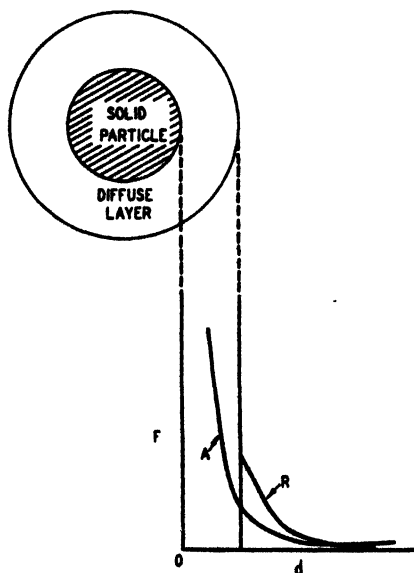


FIG. 7. A simplified picture of the nature of the forces associated with the charge of a colloidal particle, the diffuse layer, and any given charge possessing the same sign as the particle, as a function of the distance separating them.

opposite to that on the particles. A picture showing the relative magnitude of the electrical forces associated with a given colloidal particle and demonstrating how this effect can occur, may be obtained from figure 7. Line *A* represents the rate of decline of the electrical forces as one travels outward from the surface of the particle; this is due solely to the ions that give the basic charge to the particle. This is essentially a plot of K/d^2 , where d is the distance out from the surface of the particle. Line *R* represents the rate of decline of the electrical forces associated with the diffuse double layer of net opposite sign and is also a plot of the function of k/d^2 , where k is smaller in value than the K in the former expression, and the vertical axis represents the center from which all the ions of the diffuse

layer may be considered to be acting. This idea of a center of action is essentially the same as that assumed in the Helmholtz equation for the zeta potential.

Thus, since the ions in the different layers are opposite in sign, we may consider curve *A* as representing the attraction forces associated with the particle, and curve *R* as representing the repulsion forces associated with the particle toward ions of opposing sign in the dispersion medium. To be concrete we shall let curve *A* represent the effect of negative adsorbed ions and curve *R* that of positive ions.

We may observe from the diagram that up to the point of intersection the repulsion forces due to the diffuse layer predominate except at small distances out from the surface of the particle. Thus, an ion of the same sign as those in the diffuse layer cannot approach the vicinity of the particle beyond that point, since the effect of Brownian motion is relatively small. When we travel out beyond that point attraction forces, although relatively weak, are found to exist. It is a likely assumption that the kinetic energy of the individual ions is sufficient to prevent them from being restrained at this point, and hence they are moving about in random motion in the dispersion medium. However, although the forces associated between the individual ions in the dispersion medium and the ions of opposite charge on the inner layer of the colloidal particle are relatively small, considerable forces may be set up between the ions on the inner layer and the ions in the dispersion medium taken as a whole. In other words, the dispersion medium may act as an oppositely charged electrical field, which effects the condensation and the orientation of the particles (figure 8).

Since the dispersion medium may be considered as possessing an excess of ions of the same charge, due to the adsorption effects of the colloidal particles, these may interact and form groups of ions which have a greater charge associated with them, as pointed out by Gurney (18). Thus these groups may act as nuclei about which the colloidal particles may condense, owing to forces of an electrical nature. On the basis of this idea, if orientation and condensation do take place, this will occur up to the point where the attraction forces between the basic charge on the particles and the ions in the dispersion medium are balanced by the forces of repulsion between the ions in the diffuse layer and the ions in the dispersion medium. Thus a rigid gel may form, which may be made fluid by redistributing the ions in the system (by shaking); see figure 8. It is difficult to form an integrated picture of the whole process, because as orientation and condensation take place the diffuse layer surrounding the particles is probably compressed; this results in a further neutralization of the basic charge on the particles which, in turn, changes the nature of the forces surrounding them. However, it is seen that the particles of a colloidal suspension may orient under suitable conditions into fixed positions, where their behavior

is controlled predominantly by electrical forces. This orientation may then result in the condensation of the particles about the ions in the dispersion medium, so that finally coagulation is achieved. As the picture of this process depends upon the adsorption characteristics of the particles and the ions and upon the charge on the ions, we shall attempt to show how it changes with variations in these factors.

COAGULATION OF A COLLOID BY ELECTROLYTE

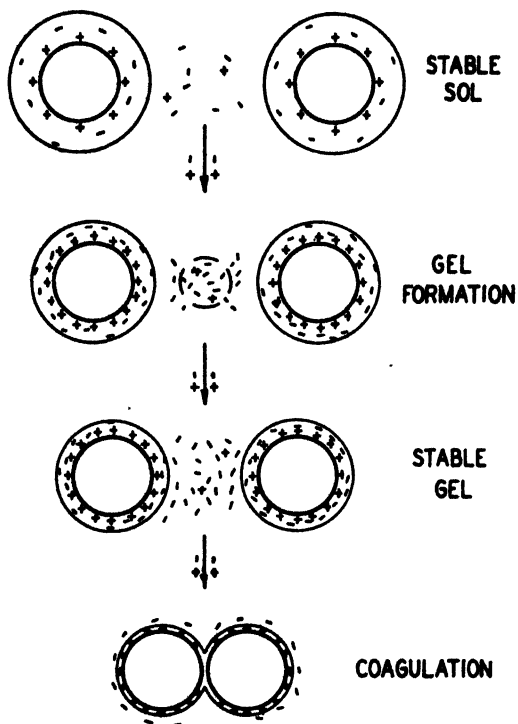


FIG. 8. Simplified picture of the mechanism of gelation and coagulation, showing the formation of an ionic field due to preferential adsorption.

It is known from experiment that to obtain the maximum gelation effects in an electrocratic colloidal system, monovalent ions that possess a sign opposite to the charge on the sol are most suitable. Furthermore, the effectiveness in this respect seems to follow the Hofmeister series. In other words, for our negative bentonite sol or a vanadium pentoxide sol, the effectiveness of the ions inducing gelation follows the series lithium, sodium, potassium, hydrogen, etc., and it is important to note that the effectiveness of the adsorption of the ion in the diffuse layer increases as we travel from lithium to hydrogen. Numerous experiments by Weiser (59) and co-

workers have shown this to hold. This would appear to show that the less strongly the ion carrying a sign opposite to that of the sol particle is adsorbed in the diffuse layer, the more powerful it is in forming gels and causing coagulation. This is in accord with the idea discussed above, for the less adsorbed the ion is, the greater tendency it has to move about in the dispersion medium and create stronger forces to exist between the sol and the dispersion medium. On the other hand, we should expect that polyvalent ions would behave altogether differently from monovalent ions. First, they would be more strongly adsorbed in the diffuse layer because of the greater electrostatic attraction and, secondly, there would be greater forces of repulsion between the ions of like sign in the dispersion medium, thus reducing any tendency of interaction of the ions to form ionic groups and making the system more diffuse. For this reason, the mechanism of coagulation should be considered as somewhat different in the case of the polyvalent ions from the case when monovalent ions are employed. Since in the case of coagulation by polyvalent ions the forces, as pointed out above, between the particles of the sol and the dispersion medium are relatively small, coagulation must be due mainly to the neutralization of the charges on the particles. This allows the particles to be impelled together by their kinetic energy, so that they may be held together by molecular forces acting at short distances of separation. This is borne out by considerable experimental data, which show that an appreciable charge exists on the particles of certain sols when coagulated by monovalent ions and practically no charge exists on the sols when they are coagulated by polyvalent ions (2) (figure 9).

Thus the electrocratic behavior of a sol depends in general upon the individual adsorption characteristics of the ions in the systems and the adsorption behavior of the colloidal substance present. Since these characteristics may vary to a great extent, one may see how it is that experimental rules, such as the Schultze-Hardy rule, for predicting the electrocratic behavior are extremely qualitative in nature.

It has been pointed out that, if monovalent ions are added to an electrocratic system where considerable preferential adsorption takes place, the effect will be a certain dependence of the behavior of the particles upon the dispersion medium. If an electric potential is placed across the system, there will be expected an electroviscous drag, caused by the dispersion medium moving toward one pole and the particles toward the other. Such an effect has already been observed by Quincke.

The experiments performed by Briggs (2) (figure 9) on the electrophoretic behavior of arsenic trisulfide sols with electrolytes may be interpreted in the light of the idea proposed above. It is seen that when potassium chloride is gradually added to the sulfide sol the electrophoretic velocity ($E. V.$) first drops, then rises through a maximum. The explanation is

as follows: When potassium chloride is added to the system, preferential adsorption of chloride ions takes place at first, leaving an excess of potassium ions in the dispersion medium. Although the charge on the particles has actually increased, a decrease in the $E. V.$ results, owing to the electroviscous effect of the dispersion medium which tends to move in the direction opposite to that of the particles. Further addition of potassium chloride presumably results in no further preferential adsorption, and therefore ions of both signs mix in the dispersion medium with the potassium ions already present. This reduces the electrical potential of the dispersion

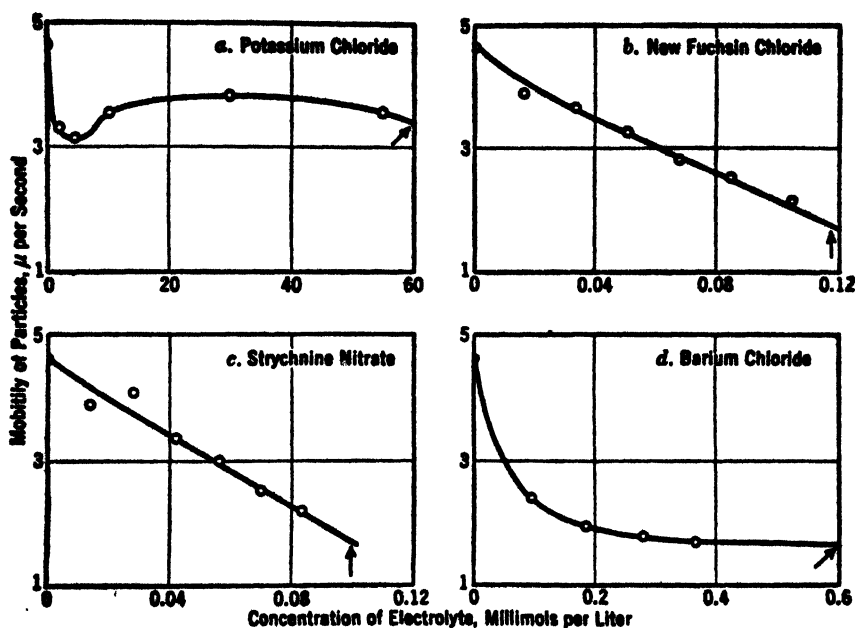


FIG. 9. Electrophoretic studies on an arsenic trisulfide sol, illustrating the effect of ions of different valence in controlling mobility and coagulation. The arrows indicate where coagulation results. (Taken from Briggs)

medium and hence the electroviscous effect is reduced. This is evidenced by an increase in the electrophoretic velocity of the particles. Finally, the concentration of potassium chloride is sufficiently large to compress the diffuse double layer surrounding the particles, so that the charge on the particles is reduced and the electrophoretic velocity drops.

As shown by the action of barium chloride, polyvalent ions behave differently. Compression of the double layer is effected from the start, owing to the greater adsorption of the barium ions in the diffuse layer. This results in a decreasing electrophoretic velocity as the salt is added.

It should be pointed out that the initial purity and concentration of the

sol will have a considerable influence on the subsequent behavior of the sol. If the sol contains a considerable amount of electrolyte to start with, then the addition of more electrolyte will result predominantly in the compression of the double layer and little preferential adsorption of ions. Or, if the sol is extremely dilute and does not contain a very large amount of electrolyte, the electrophoretic velocity of the particles may increase upon the addition of monovalent ions, owing to the reduced effect of the dispersion medium upon the sol.

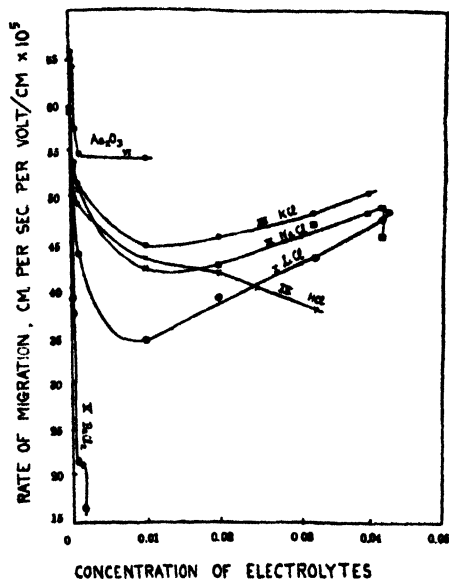


FIG. 10

Fig. 10. The effect of monovalent ions on the electrophoretic velocity of an arsenic trisulfide sol (cf. curve III with part a of figure 9). (Taken from Mukherjee)

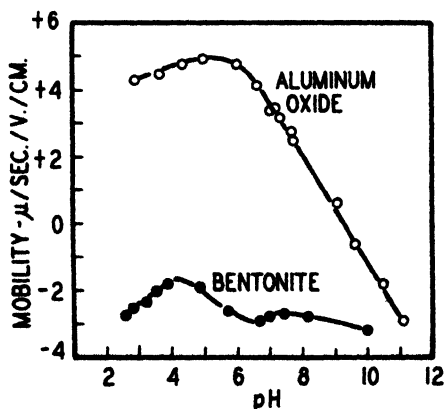


FIG. 11

Fig. 11. Effect of sodium hydroxide on the mobility of aluminum oxide sol and bentonite.

Data reported by Mukherjee *et al.* (37) (figure 10) show that, in a purified sol which exhibits preferential adsorption of the anion, the addition of lithium, sodium, and potassium salts initially causes the electrophoretic velocity to go through a minimum. The greatest initial reduction in electrophoretic velocity occurs with lithium as counter ion. In accordance with the order mentioned, the potassium ion results in the least reduction. This order agrees closely with the adsorptive power of the ions in accordance with the Hofmeister series, where the lithium ion is the least adsorbed. Thus the effect produced is just what would be predicted from the theory.

Also in line with this idea are the experiments of Hazel (23) (figure 11) in regard to the behavior of the electrophoretic velocity of bentonite

particles with the concentration of sodium hydroxide. The initial reduction in the electrophoretic velocity may be attributed to the replacement of the hydrogen ions, which react with the hydroxide ions to form water, by the sodium ions, which are adsorbed to a lesser extent in the diffuse layer and are more easily ionized from the bentonite particles. Thus, a considerable electroviscous effect is produced by the increase of the electric potential of the dispersion medium.

The increase in electrophoretic velocity that follows is due to the addition of the negative hydroxide ions as well as the positively charged sodium ions to the dispersion medium, since at this point, as is indicated by the pH value of 6.8, the majority of the hydrogen ions have reacted to form water. Thus the electroviscous effect of the dispersion medium is reduced.

Presumably the repression of the ionization of the sodium ions from the bentonite particles, due to the increasing concentration of the electrolyte, is the cause of the second decrease in mobility, and the final increase in the electrophoretic velocity is probably due to the adsorption of hydroxide ions on the bentonite particles at the high pH values.

At a pH of 4.5 the charge on the particles may well be a maximum even though the electrophoretic velocity is a minimum, since the minimum is due to the electroviscous effect and not to a reduction in charge. The Helmholtz-Gouy equation may not yield the correct particle charge, because it does not take into account the effect of the dispersion medium in controlling the behavior of the sol.

In the same diagram the electrophoretic velocity of the aluminum oxide is seen to increase through a maximum, presumably only because the sol is too dilute for the limited amount of preferential adsorption to result in a measurable minimum electrophoretic velocity. This type of curve is similar to those obtained on negative platinum sols by Pennycuik (44) (figure 12).

The Burton and Bishop (3, 4) rule, which states that, in general, for monovalent coagulating ions the precipitation ratio increases with decreasing concentration of the sol and with polyvalent coagulating ions the flocculation value decreases with decreasing concentration of the sol, can well be correlated with our concept of the mechanism of coagulation with different valence ions (figure 13). (Although Weiser and Nicholas (58) claim that the rule does not always hold, in view of the behavior of hydrous oxide sols, recently Ghosh and Dhar (15) have shown that when these sols are sufficiently purified they follow the rule.) In the case of coagulation with monovalent ions in the concentrated sol, the preferential adsorption of one ion causes the particles to condense about various points in the dispersion medium. Also, at the same time compression of the diffuse double layer occurs. Thus when complete coagulation occurs, all the ions in the sol take part. On the other hand, in the dilute sol the particles are

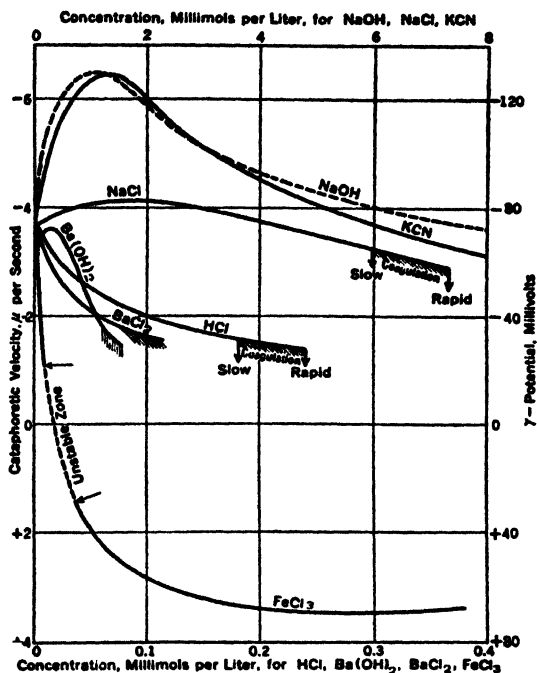


FIG. 12. The effect of various ions on the electrophoretic velocity of colloidal platinum. (Taken from Pennycuik)

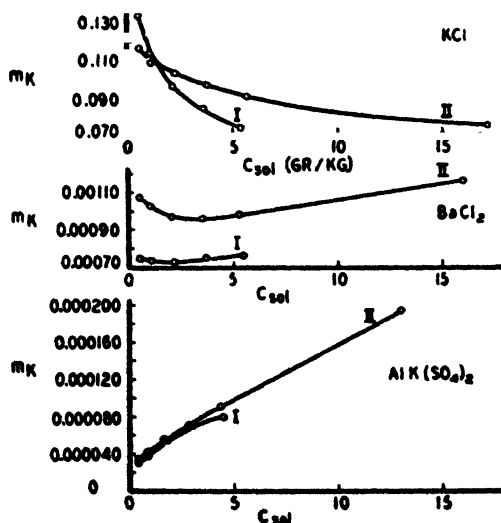


FIG. 13. The effect of the concentration of a sol on the coagulation value of ions of different valence. (Taken from Ostwald)

less dependent on the forces in the dispersion medium and coagulation must take place primarily by the reduction of the charge due to the adsorption of ions of opposite sign. To effect the adsorption of a sufficient number of ions, a larger concentration of electrolyte is required in the dilute sol.

On the other hand, the decrease in the flocculation value obtained by dilution of the sol with polyvalent coagulating ions is what is to be expected, since coagulation in any case occurs mainly by the neutralization of the charge on the individual particles by adsorption of the polyvalent ions, the extent of which is determined by the concentration of the ions in the solution. When coagulation occurs in the concentrated sol, the agglomerated particles entrain considerable electrolyte from the solution, requiring more electrolyte to coagulate the remaining particles. In dilute solution there

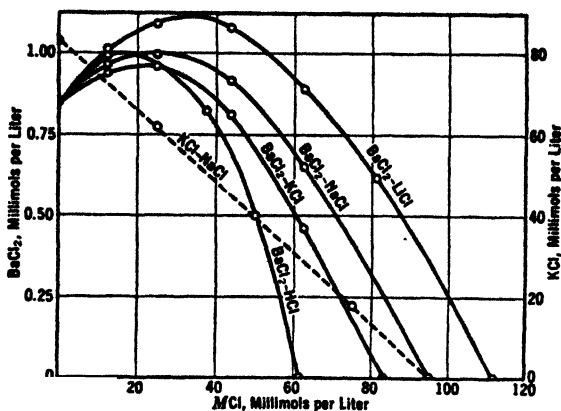


FIG. 14. Influence of ion antagonism exhibited by mixtures of salts on the coagulation value of an arsenic trisulfide sol. (Taken from Weiser)

is relatively little entrainment, so that there is a decrease in precipitation value.

The phenomenon of ion antagonism, which was originally observed by Linder and Picton (32) and which has been extended more recently by Chaudhury and Sen-Gupta (5), Rabinerson (47), Weiser (55), and others, may be interpreted in view of the concept proposed above. As shown in figure 14, the coagulation of the arsenic trisulfide sol with the salt pairs involving bivalent and monovalent coagulating ions requires a precipitating power that is greater than that of each salt alone. We may visualize the process in this way: If we add a small amount of monovalent coagulating ion to the sol, then presumably the kinetic energy of the particles will decrease, owing to the increased dependence of the particles upon the forces in the dispersion medium. Since coagulation by polyvalent ions is mainly controlled by the reduction of the charge of the

particle to a critical point where the kinetic energy of the particles may be effective in coagulating one particle with another, then with a reduction of the kinetic energy of the particles the charge on the particles must also be reduced further to effect coagulation. So for coagulation to ensue, a greater amount of precipitating power of the polyvalent ion is required than under normal conditions.

The theory proposed herewith appears to correlate well with a great variety of existing experimental data, and therefore may offer a new means of predicting the behavior of electrocratic sols and a better understanding of the gelation and coagulation of electrocratic colloidal dispersions in general.

REFERENCES

- (1) BASINSKI: *Roczniki Chem.* **15**, 430 (1935).
- (2) BRIGGS: *J. Phys. Chem.* **34**, 1326 (1930).
- (3) BURTON AND BISHOP: *J. Phys. Chem.* **24**, 701 (1920).
- (4) BURTON AND BISHOP: *J. Phys. Chem.* **25**, 517 (1921).
- (5) CHAUDHURY AND SEN-GUPTA: *J. Indian Chem. Soc.* **14**, 133 (1937).
- (6) DEBYE AND HÜCKEL: *Physik. Z.* **24**, 185 (1923).
- (7) DEBYE AND HÜCKEL: *Physik. Z.* **25**, 49 (1924).
- (8) DESAI AND BARVE: *Nature* **128**, 907 (1931).
- (9) DESAI AND BARVE: *Trans. Faraday Soc.* **29**, 1269 (1933).
- (10) DUCLEAUX: *J. chim. phys.* **5**, 36 (1907).
- (11) FREUNDLICH AND LEONHARDT: *Kolloid-Beihefte* **7**, 195 (1915).
- (12) FREUNDLICH: *Thixotropy*, p. 13. Paris, Hermann et Cie. (1935).
- (13) GHOSH: *J. Chem. Soc.* **26**, 93 (1929).
- (14) GHOSH AND DHAR: *J. Phys. Chem.* **31**, 187 (1927).
- (15) GHOSH AND DHAR: *J. Indian Chem. Soc.* **10**, 475 (1933).
- (16) GOODEVE: *Trans. Faraday Soc.* **35**, 3421 (1939).
- (17) GOUY: *J. phys. radium* **9**, 457 (1910).
- (18) GURNEY: *J. Chem. Phys.* **6**, 499 (1938).
- (19) HAMAKER: *Rec. trav. chim.* **55**, 105, 1547 (1936).
- (20) HARTLEY: *Trans. Faraday Soc.* **31**, 31 (1935).
- (21) HAUSER AND LEBEAU: *J. Phys. Chem.* **42**, 961 (1938).
- (22) HAUSER AND REED: *J. Phys. Chem.* **41**, 929 (1937).
- (23) HAZEL: *J. Phys. Chem.* **42**, 409 (1938).
- (24) HAZEL AND McQUEEN: *J. Phys. Chem.* **37**, 553, 571 (1933).
- (25) HELMHOLTZ: *Wied. Ann.* **7**, 337 (1879).
- (26) HOUWINK: *Elasticity, Plasticity and Structure of Matter*, p. 352. University Press, Cambridge (1937).
- (27) KALLMAN AND WILLSTÄTTER: *Naturwissenschaften* **20**, 952 (1932).
- (28) KRUYT: *Trans. Faraday Soc.* **31**, 28 (1935).
- (29) LANGMUIR: *J. Chem. Phys.* **6**, 873 (1938).
- (30) LANGMUIR: *Proc. Roy. Soc. (London)* **A170**, 1 (1939).
- (31) LEVINE: *Proc. Roy. Soc. (London)* **170**, 145, 165 (1939).
- (32) LINDER AND PICTON: *J. Chem. Soc.* **67**, 67 (1895).
- (33) MARSHALL: *Z. Krist.* **90**, 8 (1935).
- (34) McMILLEN: *J. Rheol.* **3**, 75 (1932).
- (35) McTAGGART: *Phil. Mag.* **27**, 297 (1914).

- (36) MUKHERJEE: *Trans. Faraday Soc.* **16**, 103 (1921).
- (37) MUKHERJEE, ROYCHOUDHURY, AND RAJKUMAR: *J. Indian Chem. Soc.* **10**, 27 (1933).
- (38) MUKHERJEE: *Kolloid-Z.* **62**, 257 (1933).
- (39) NICOLARDOT: *Ann. chim. phys.* **6**, 362 (1905).
- (40) OSTWALD: *Kolloid-Z.* **73**, 301 (1935).
- (41) OSTWALD: *J. Phys. Chem.* **42**, 986 (1938).
- (42) PAULI AND MATULA: *Kolloid-Z.* **21**, 49 (1917), et seq.
- (43) PAULI AND VALKO: *Z. physik. Chem.* **121**, 161 (1926).
- (44) PENNYCUICK: *J. Chem. Soc.* **1930**, 1447.
- (45) PRYCE-JONES: *J. Oil Colour Chem. Assoc.* **17**, 305-75 (1934).
- (46) QUINCKE: *Pogg. Ann.* **113**, 513 (1861).
- (47) RABINERSON: *Kolloid-Z.* **42**, 50 (1927).
- (48) RABINOWICH AND KARGIN: *Trans. Faraday Soc.* **31**, 50 (1935).
- (49) ROBINSON: *Proc. Roy. Soc. (London)* **170**, 519 (1939).
- (50) SCHALEK AND SZEGVARI: *Kolloid-Z.* **33**, 326 (1923).
- (51) SEN: *J. Phys. Chem.* **29**, 354 (1925).
- (52) SEN: *J. Indian Chem. Soc.* **3**, 8 (1924).
- (53) SORUM: *Kolloid-Z.* **58**, 314 (1932).
- (54) SORUM AND FISHER: *J. Phys. Chem.* **24**, 70 (1920).
- (55) WEISER: *J. Phys. Chem.* **28**, 232 (1924).
- (56) WEISER: *J. Phys. Chem.* **29**, 955 (1925).
- (57) WEISER: *Inorganic Colloid Chemistry*, Vol. II, p. 76. John Wiley and Sons, Inc., New York (1938).
- (58) WEISER: *Inorganic Colloid Chemistry*, Vol. III, p. 192. John Wiley and Sons, Inc., New York (1938).
- (59) WEISER, MILLIGAN, AND COPPOC: *J. Phys. Chem.* **42**, 427 (1938).
- (60) WEISER AND NICHOLS: *J. Phys. Chem.* **25**, 742 (1921).

STUDIES IN GELATION AND FILM FORMATION. II

STUDIES IN CLAY FILMS¹

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In a previous publication (5) it was demonstrated that self-supporting, coherent films could be obtained from bentonite gels³ by spreading the gels on an appropriate support and drying them in this condition. The films so obtained have become generally known as Alsifilm (*aluminum silicate film*). Since they are entirely composed of pure clay, they offer a new and interesting condition of matter for colloidal studies.

PARTICLE SIZE VS. WATER CONTENT OF DRY FILM

Instead of producing crude Alsifilm from a polydisperse gel (a gel containing particles of different sizes but all of colloidal dimensions), it was found that films produced from monodisperse gel fractions (7, 14) retained different amounts of water. These variations are shown graphically in figure 1. The results demonstrate that the water content of the films increases with decreasing size of the original particles. This would agree with previously reported data on the amount of water adsorbed on clay particles of fractions of different sizes present in a sol (6).

For the determination of the total water content of a clay particle we must also consider the osmotically imbibed water. In this connection it has been found that the withdrawal of the osmotically imbibed water from clay gels is easier, the smaller the original particles (2). This is in

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³ The term "bentonite" as used in this paper refers, unless specifically indicated otherwise, to the colloidal-sized particles of the swelling type of the mineral montmorillonite, which constitutes the major part of our natural bentonite deposits. All impurities and supercolloidal particles have been removed from the systems used in this work, either by sedimentation or by supercentrifuging. For the present studies a bentonite mined in Wyoming was used exclusively. It is a sodium hydrous aluminum silicate. However, identical results have been obtained with hydrous magnesium silicates having alkali cations as counter ions attached to the complex colloidal anion.

agreement with the experimental fact that coherent self-supporting films can be more quickly produced from gels containing fine particles. This, however, would indicate that such films, having once been deposited to a coherent structure, should have the smallest amount of retained water. One can explain this apparent discrepancy by accepting the structure for montmorillonite as postulated by Hofmann, Endell, and Wilm (9) and by assuming one of the following theoretically conceivable possibilities as to

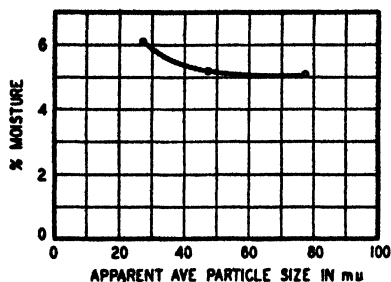


FIG. 1. Moisture content of crude Alsifilm *versus* particle size of original bentonite gel

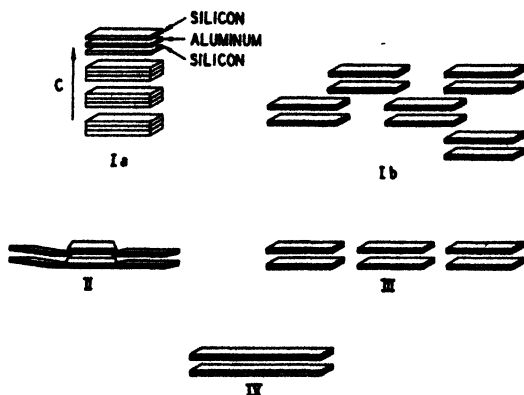


FIG. 2. Theoretical possibilities in the formation of large clay particles. Ia, growth by stacking of unit layer parcels along the *c*-axis of the unit crystal; Ib, growth by stacking simultaneously along at least two axes of the unit crystal; II, random agglomeration of unit crystals; III, alignment of unit crystals along the *a*-axis or the *b*-axis by micellar cohesion forces; IV, originally large crystals.

the difference in particle sizes (figure 2): (I, a and b) The larger particles consist of a multitude of layer parcels stacked together in the direction of at least one axis of the unit crystal. (II) The larger particles are randomly oriented agglomerates of layer parcels. (III) A series of unit layer parcels is held together in chain formation in the direction of the *a*- and *b*-axes of the unit crystal, thus forming fibrillar aggregates. (IV) The presence of particles with the original *a*-axis or *b*-axis extended.

In all these cases it will be more difficult to withdraw the imbibed water from the film made up originally of small particles than from the gel, because decreasing original particle size increases the capillary interstices in the film structure. This is substantiated by the fact that films produced from fractions of fine particle size show no change in water content even after prolonged storage in air, whereas films made under identical conditions from fractions of coarse particle size exhibit a noticeable drop in water content during the first days of storage.

The formation of Alsifilm is the result of the particles present in the gel lining up in some way and forming fibrillar interweaving crystalline aggregates.

INFLUENCE OF TEMPERATURE

Further proof of the above discussion is offered by the fact that films that have been dehydrated once at different temperatures (110°, 180°, 250°, 400°, 550°C.) will pick up the same amount of moisture if placed in

TABLE 1
Moisture content of bentonite films versus temperature

TEMPERATURE	MOISTURE CONTENT		
	76 m μ *	47 m μ *	27 m μ *
°C.	per cent	per cent	per cent
110	5.1	5.0	5.0
180	2.7	2.8	2.7
250	1.9	1.9	1.9
400	1.3	1.4	1.4
550	0.8	0.8	0.8

* Apparent original particle size.

air (40 per cent moisture content) irrespective of their original particle size. The results are recorded in table 1. Such films, if brought in contact with water, will swell visibly, eventually be reconverted to a gel, and finally peptize to the sol condition.

Films that have been heated up to 700°C. and 800°C. will no longer pick up water either from the surrounding atmosphere or if immersed in water.

These facts substantiate previous observations that the colloidal properties of the bentonitic clay particle remain practically unaltered up to about 700°C. At higher temperatures a complete collapse of the lattice prevents osmotic imbibition.

An interesting, but so far not yet fully explainable phenomenon is the fact that films deposited from electrodialyzed or hydrogen bentonite pick up nearly twice as much water as regular crude Alsifilm, inasmuch as they

have not been subjected to temperatures above 250°C. The results are recorded in table 2. The most probable reason for this phenomenon is that an irregular agglomeration of the clay particles takes place during their transformation into hydrogen bentonite. The agglomerates would again tend to include larger quantities of water. The tendency to agglomerate and form clusters has been verified by ultramicroscopic observations.

TABLE 2
Moisture content of hydrogen bentonite film versus temperature
Apparent original particle size = 47m μ

TEMPERATURE	MOISTURE CONTENT
°C.	per cent
25	10.9
110	6.5
250	2.3
400	1.3
550	0.8

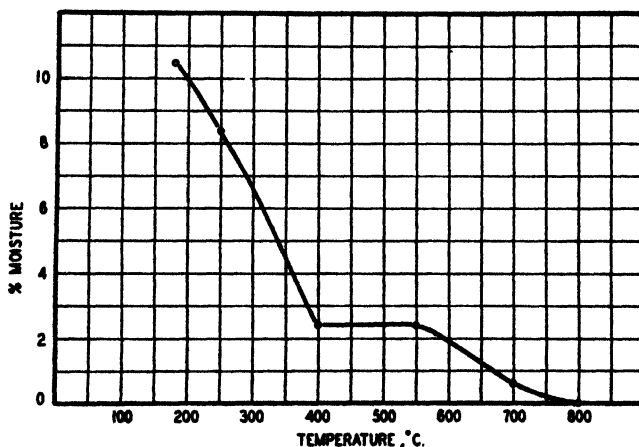


FIG. 3. Moisture pick-up of Alsifilm in water made from hydrogen bentonite after having been heated to different temperatures.

It has long been known that hydrogen bentonite, if once fully desiccated, can no longer be redispersed in water. This phenomenon can be demonstrated nicely with hydrogen bentonite films. Figure 3 shows the water pick-up of such films, which had been heated to various temperatures for 18 hr., then placed in water at 25°C. for 48 hr., and air-dried, in comparison with the pick-up by regular films. Even the films that have been heated to temperatures below 180°C. do not redisperse, but they are too fragile to be handled as coherent sheets.

Presumably what happens during progressive dehydration is that two unit parcels are forced so close to each other that the forces acting between them become predominant. The relatively low temperatures needed to bring about such a change could be explained by the fact that the hydrogen ion is the least hydrated ion.

INFLUENCE OF ELECTROLYTES ON THE CRUDE FILM

Most interesting of all reactions is the influence of different electrolytes on the properties of Alsifilm. The well-known fact that swellable sodium montmorillonite exhibits a large base-exchange capacity in comparison with the non-swelling types (fullers' earth) or with kaolinites led to experiments to determine whether such base exchange could also be accomplished if the clay were present in film form. For this purpose crude Alsifilm was immersed in saturated solutions of different electrolytes.

TABLE 3
Moisture content of films treated with potassium hydroxide

FILM	MOISTURE CONTENT		
	76 m μ *	47 m μ *	27 m μ *
	per cent	per cent	per cent
Original film.....	5.4	5.5	6.1
Film treated with potassium hydroxide .	4.4	4.7	4.7
Film heated to 110°C. after treatment. ..	0.3	0.6	0.6
After immersion in water.....	7.2	7.3	7.8

* Apparent original particle size.

The use of saturated solutions, or at least highly concentrated ones, is necessary in this case, as otherwise the film would peptize prematurely. This means that base exchange must take place in the presence of a concentration of cations such that neutralization of the particle charge at the same time is guaranteed.

Alsifilm immersed for 12 hr. (at 25°C.) in a saturated solution of potassium hydroxide showed upon analysis complete replacement of the sodium originally present. The moisture content dropped from 5.4 per cent in the original film to 4.4 per cent after treatment and to only 0.3 per cent after heating the treated film to 110°C. for 18 hr., i.e., its moisture content was far below that of the original dry clay. Even when a film so treated had been immersed in water for 2 days, it had picked up only 7.2 per cent. The film no longer swelled and remained absolutely coherent. Films made from originally finer dispersions resulted, as was to be expected, in slightly higher figures for moisture content, but the values were still of the same order of magnitude. The results are given in table 3.

With lead acetate we again obtain complete exchange of the sodium and the small amount of potassium present in the natural material. In this case the water content of 5.4 per cent of the original film dropped to 2.4 per cent after treatment and to 0.5 per cent after having been heated to 110°C. for 18 hr. After immersion in water for 2 days the treated and heated films showed a moisture content of 8.8 per cent. Again, no signs of swelling and disintegration were observed, the films being absolutely resistant to the influence of water for many months. Results obtained with fractions of finer particle size again lie slightly higher. The results are recorded in table 4.

The treatment of crude Alsifilm with other electrolytes, as, for example, silver, resulted in complete base exchange, but these films were not water-resistant (for an explanation, see below).

It is interesting to note that small amounts of magnesium could *always* be detected in the treating bath (prepared from c.p. chemicals and con-

TABLE 4
Moisture content of films treated with lead acetate

FILM	MOISTURE CONTENT		
	76 m μ *	47 m μ *	27 m μ *
	per cent	per cent	per cent
Original film.....	5.4	5.5	6.1
Film treated with lead acetate.....	2.4	2.8	2.9
Film heated to 110°C. after treatment. . .	0.5	0.7	0.8
After immersion in water.....	8.7	8.9	8.9

* Apparent average particle size.

ductivity water) after treatment of crude films. This indicates that measurable quantities of magnesium have been removed during treatment. Since the presence of magnesium as counter ion is highly improbable, however, its presence in the lattice being an accepted possibility (11, 12), this fact seems to substantiate the findings of Kelley, Dore, Brown, and Jenny (10, 11), who were able to remove from bentonite, ground for a prolonged time, increasing quantities of magnesium and potassium. An x-ray analysis of the ground material showed a partial destruction of the crystal lattice. In the present case, also, a marked change in structure was found by x-ray and microscopic analysis.

Another fact of interest is the amount of cation retained by treated films deposited from fractions of different particle sizes. It was found in the case of lead acetate that the films produced from a particle size range of 67 to 85 m μ retained 12.13 per cent lead, those made up of particles ranging from 44 to 50 m μ retained 14.18 per cent, and those of particles

between 24 and 30 $m\mu$ retained 15.16 per cent lead. A film deposited from hydrogen bentonite of the finest fraction retained even 20.7 per cent of lead. This fact is in contradiction to the data given by E. A. Hauser and C. E. Reed (8), who found that the total base-exchange capacity of bentonite in dispersion was practically independent of particle size. No fully satisfactory explanation for this discrepancy can yet be offered. However, the loose network structure of crude bentonite films, as demonstrated by ultramicroscopic studies (5), might offer an answer. The fabric-like structure is denser when depositing a film from fractions of fine particle size than from fractions of coarse particle size. This makes increasing mechanical inclusion highly probable.

STRUCTURE OF FILMS

The reactivity of the crude film finds its explanation in an extensive x-ray study, to be published in detail in the near future. Diffraction patterns obtained by x-ray radiation perpendicular and parallel to the plane of the film have demonstrated that the unit crystals lie with their *c*-axis perpendicular or at a slight angle to the plane of the film, so that the individual lattice layers must lie parallel or at a slight angle thereto. Reverting to the four theoretical possibilities as to the difference in particle size, we are now in a better position to consider their probability. The fact that crude films when immersed in water swell predominantly in regard to their thickness would conform to all possibilities.

Possibility IV can be eliminated, as large particles would have to be detectable by microscopic observation and sedimentation analysis.

Possibility II seems highly improbable, because the presence of unoriented agglomerates would call for unoriented growth upon desiccation; moreover their presence would be detectable. This would be contrary to the observed film structure.

Possibility III must be considered as likely, especially if one accepts the recent theories of gelation and alignment, as only such an assumption would explain the loose coherence of particles surrounded by ionic atmospheres of identical charge.

On the basis of all the reactions possibility I seems to furnish the most plausible explanation of the formation of the film structure. From the two theoretical possibilities schematically shown in parts Ia and Ib of figure 2, the stacking of unit crystals according to Ib seems the most probable configuration. This arrangement is the only one that is able to explain the phenomenon observed when a thin strip of the film is hammered in its middle with the edge of a ruler. The film bends on both free ends, owing to displacement of the stacks against each other when impacted. If the film is then turned over and the procedure repeated, it will flatten out first and then bend upward in the opposite direction as before.

A film that has been previously treated with electrolytes and been made water-resistant thereby will no longer show this phenomenon. This is in full agreement with the explanation offered for water resistance as schematically demonstrated in figure 4b.

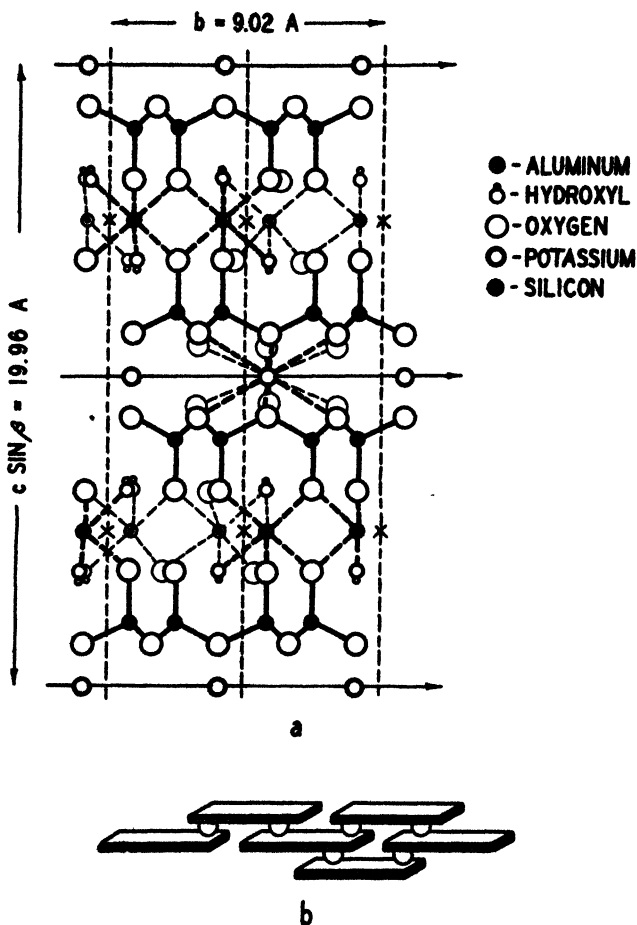


FIG. 4. (a) Schematic drawing of the structure of mica (muscovite) projected at a plane normal to the a -axis (from W. L. Bragg). (b) Probable bonding of unit layer parcels by large cations in water-resistant Alsifilm.

A combination of possibilities I and III is equally conceivable and would also be in accord with the facts so far discussed.

The fact that films treated with certain electrolytes lose their ability to swell appreciably or to redisperse completely, whereas the treatment with other electrolytes results only in base exchange, is of importance. A careful study of the cations causing water resistance and those which do

DISCUSSION AND INTERPRETATION OF THE THERMODYNAMIC PROPERTIES, CONDUCTIVITY, AND DIFFUSION OF A TYPICAL COLLOIDAL ELECTROLYTE: LAURYL-SULFONIC ACID IN AQUEOUS SOLUTION¹

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I. INTRODUCTION

The exact quantitative interpretation of the various properties of colloidal electrolytes meets with a number of difficulties, and progress is possible only through the use of drastic simplifications and assumptions. Any theory that tries to take account of more factors than can be handled simultaneously by rigorous methods will never reach a stage where significant comparison with experimental data can be carried out. On the other hand, simplifying assumptions should be systematically applied to the interpretation of the data before any opinion as to the respective merits and defects of these assumptions is expressed. The method should be the following: Having at one's disposal reliable data corresponding to one or several properties of the systems under consideration, one sets up the exact equations describing these properties according to the simplifying assumptions previously adopted. These equations are written for a number of different concentrations, and solved for the unknowns corresponding to the assumptions chosen; for instance, as in the work discussed in the present paper, the numbers of positive and negative simple ions associated in the average micelle. If the equations are compatible, and if their solutions are at all plausible, something tangible with some element of truth has probably been obtained. One at least knows exactly "where one stands" regarding the assumptions at the basis of the treatment. The present confusion of the subject and the conflicting theories so far proposed should be clarified to some extent by the use of the method here suggested. In a previous paper (16) the author has tested in this manner the application of the Debye-Hückel theory to the interpretation of osmotic data of two colloidal electrolytes, Congo red and sodium thymonucleate, in aqueous solution, the assumption being that a negative micelle with a large charge is present. The equations were solved for

¹ Presented at the Sixteenth Colloid Symposium, held at Stanford University, California, July 6-8, 1939.

the ionic diameter a of the Debye-Hückel theory, the charge of the negative micelle being assumed constant but large enough to make the function $\sigma(ka)$ of the theory smaller than unity, as required to make a positive. When a turned out to be fairly constant over the whole range of concentrations, a reasonable model for the electrolyte was assumed to have been obtained. The method, in spite of several imperfections, works in the right direction and explains, at least qualitatively, the very low osmotic pressures exhibited by these electrolytes. The assumptions involved in such a treatment have been discussed by Hartley (2). Very recently, the main ideas of the Debye-Hückel theory have been applied by Levine

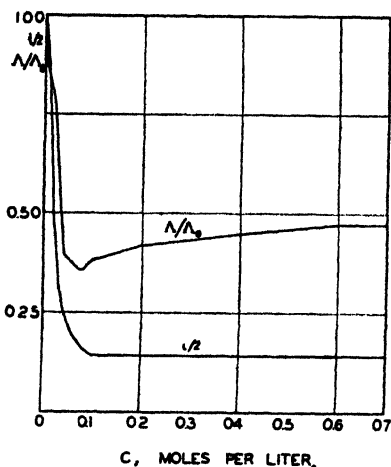


FIG. 1

FIG. 1. Variation with concentration of the osmotic coefficient and of the conductivity ratio of aqueous solutions of laurylsulfonic acid.

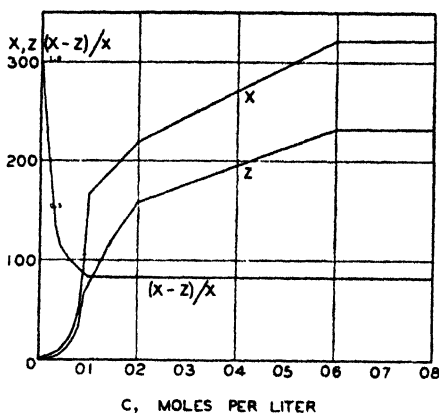


FIG. 2

FIG. 2. Number (x) of laurylsulfonate ions and number (z) of hydrogen ions in the average micelle of laurylsulfonic acid solutions. Apparent degree of ionization $= ((x - z)/x)$.

(6) to the problem of stability in hydrophobic colloidal solutions. The Debye-Hückel theory is also used in the theoretical considerations recently published by Langmuir (5).

At the suggestion of Professor McBain we have attempted to interpret the properties of aqueous solutions of lauryl (or dodecyl) sulfonic acid, for which conductivities (10), freezing points (11), and electromotive forces (12) have been measured by McBain and Betz, and diffusion coefficients by Mrs. McBain (7). Further conductivity and freezing point data are reported in a recent paper by Mrs. McBain, Dye, and Johnston (8). On figure 1 are plotted the osmotic coefficients, i , and the molar conductivities, Λ . The i values correspond to van't Hoff's definition and are deduced

for round concentrations from Johnston's data by means of linear interpolation between consecutive experimental points. At concentrations larger than 0.1 we have assumed i constant and equal to its value 0.280 at 0.1, while McBain and Betz' values for the range 0.1 to 0.8 vary from 0.326 to 0.318, with a minimum of 0.290 at a concentration of 0.36. Differences of this order have a negligible influence on our calculations. The Δ values are those of Mrs. McBain (8) and of Betz (9), obtained at 25°C. These are used in conjunction with i values corresponding to the freezing point.

The presence of colloidal micelles in these solutions is obvious and, without adopting any *a priori* assumption as to the possible presence of several types of micelles, we shall attempt to account for these two properties (osmotic coefficient and conductivity) on the basis of an average micelle whose composition changes with concentration. The results will then be used in a discussion of diffusion coefficients. Although interionic forces are undoubtedly at play, their effect is certainly small compared with the ideal properties of the associative model, just as in the case of dilute strong electrolytes ideality in terms of complete dissociation is responsible for the main portion of the thermodynamic properties. With many colloidal electrolytes the model is still to be found, and refinements or corrections taking electrostatic and other forces into account have but little significance as long as the problem of finding the correct model is not solved.

Ideality implies constancy of mobilities for the simple ions. The mobility of the average micelle, however, changes with size and charge. We shall calculate this mobility according to Stokes' law, along the lines suggested long ago by McBain (9). A *posteriori* interpretation of diffusion data seems to confirm the validity of this application of Stokes' law.

II. OSMOTIC COEFFICIENTS AND CONDUCTIVITIES OF LAURYL SULFONIC ACID IN AQUEOUS SOLUTION EXPLAINED ON THE BASIS OF AN AVERAGE NEGATIVELY CHARGED MICELLE

At each concentration we assume that we have exclusively an "average micelle," H_zL_x , consisting of z hydrogen ions (H^+) and x laurylsulfonate ions (L^-), together with the compensating amount of free hydrogen ion. The charge $x - z$ of the micelle is balanced by that of $x - z$ free hydrogen ions. Calling C the total concentration of acid in moles per liter of HL (exact formula: $HC_{12}H_{25}SO_3$), and designating by (H^+) and (H_zL_x) the respective concentrations of free ions and micelles, we have the following two stoichiometric conditions:

$$(H^+) + z(H_zL_x) = C \quad (1)$$

$$x(H_zL_x) = C \quad (2)$$

The osmotic coefficient, i , is such that

$$(H^+) + (H_sL_s) = iC \quad (3)$$

We shall assume that this law, strictly valid only at low concentrations, applies to the whole range of concentrations considered here, i. e., up to 0.8 molar. Calling Λ_+ and Λ_- the molar conductivities of H^+ and H_sL_s , the molar conductivity, Λ , of the electrolyte is such that

$$(H^+)\Lambda_+ + (H_sL_s)\Lambda_- = C\Lambda \quad (4)$$

For each particular concentration C we have four unknowns: x , z , (H^+) , and (H_sL_s) , but we also have four independent equations. Let us note that any incomplete dissociation is automatically taken into account in the average micelle. This likewise includes any free simple sulfonate ions. A treatment of this type could actually be developed for an electrolyte like acetic acid, for which one would find an average negative ion intermediate between the acetate ion and the neutral acetic acid molecule, the charge of this "average ion" being a function of the total concentration.

In formula 4 we shall take $\Lambda_+ = 350$, the limiting value of the molar conductivity of hydrogen ion at infinite dilution at 25°C. For the simple laurylsulfonate ion, i. e., when $x = 1$, $z = 0$, we have $\Lambda_- = 22$, according to the latest experimental data from this laboratory (8).

On the basis of Stokes' law the mobility $u(x, z)$ of the micelle in centimeters per second per unit field is

$$u(x, z) = \frac{(x - z)\epsilon}{6\pi\eta r(x, z)} \quad (5)$$

in which ϵ is the elementary charge of positive electricity, η is the viscosity of the medium, and $r(x, z)$ is the radius of the micelle which is assumed to be spherical. The mobility $u(1, 0)$ of the simple ion is

$$u(1, 0) = \frac{\epsilon}{6\pi\eta r(1, 0)} \quad (6)$$

From equations 5 and 6, neglecting the variation of viscosity, we deduce

$$u(x, z) = (x - z) \frac{r(1, 0)}{r(x, z)} u(1, 0) \quad (7)$$

The volume of the micelle is proportional to the number (x) of laurylsulfonate ions and is practically independent of the number (z) of hydrogen ions. Hence

$$\frac{r(1, 0)}{r(x, z)} = \frac{1}{x^{1/3}} \quad (8)$$

and, according to equation 7,

$$u(x, z) = \frac{x - z}{x^{1/3}} u(1, 0) \quad (9)$$

The molar conductivity of the micelle is then related to that of the simple ion by the formula

$$\Lambda(x, z) = \frac{(x - z)^2}{x^{1/3}} \Lambda(1, 0) \quad (10)$$

Equation 4 becomes

$$350(\text{H}^+) + 22 \frac{(x - z)^2}{x^{1/3}} (\text{H}_2\text{L}_2) = \Lambda C \quad (11)$$

Combining equations 1 and 3 we get

$$z = (1 - i)x + 1 \quad (12)$$

One easily finds that

$$(\text{H}^+) = C \left(i - \frac{1}{x} \right) \quad (13)$$

$$(\text{H}_2\text{L}_2) = \frac{C}{x} \quad (14)$$

Taking equations 12, 13, and 14 into account in equation 11, we get

$$350 \left(i - \frac{1}{x} \right) + 22 \frac{(ix - 1)^2}{x^{4/3}} = \Lambda \quad (15)$$

or, also,

$$\frac{1}{x^{4/3}} (0.063i^2 x^2 - 0.126ix - x^{1/3} + 0.063) = \frac{\Lambda}{350} - i \quad (16)$$

This equation is solved by successive approximations for a number of round concentrations. The particular concentration for which the difference $\frac{\Lambda}{350} - i$ is equal to zero (0.058 molar) is also included. From x and i one calculates z by means of formula 12 and the concentrations (H^+) and (H_2L_2) by means of formulas 13 and 14. The results are reported in table 1, in which are recorded, in successive columns, the stoichiometric molar concentration, the osmotic coefficient, i , the molar conductivity, Λ , the values of x , those of z , and the concentrations (H_2L_2) and (H^+) . The values of x and z , as well as those of $(x - z)/x$, are plotted on figure 2. The latter values are a measure of the relative charge of the

micelle; they also represent the ratio of the hydrogen-ion concentration to the total concentration:

$$\alpha = \frac{x - z}{x} = \frac{(H^+)}{C} \quad (17)$$

The concentrations (H_2L_x) and (H^+) are plotted (at different scales) on figure 3. The results are entirely acceptable. The maximum in the (H_2L_x)-curve is due to the combined effect of two factors: increase of concentration of the simple ions and increasing size of the micelles, our H_2L_x being an average of all micelles, molecules, and simple sulfonate ion.

TABLE 1

Composition of the "average inclusive micelle" and concentrations of that micelle and of the hydrogen ion in aqueous solutions of laurylsulfonic acid, assuming no other constituents to be present

<i>C</i>	<i>i</i>	Λ	<i>z</i>	<i>s</i>	(H_2L_x)	(H^+)
0	2.000	372	1.00	0.00	0	0
0.005	1.872	330	1.02	0.11	0.00490	0.00446
0.01	1.760	323	1.16	0.12	0.00862	0.00897
0.02	0.990	246	2.91	1.03	0.00687	0.01292
0.03	0.640	168	5.09	2.83	0.00589	0.01332
0.04	0.512	147	7.80	4.81	0.00513	0.01532
0.05	0.432	142	13.8	8.81	0.00363	0.01800
0.058	0.396	139	18.9	12.4	0.00307	0.01995
0.06	0.388	137	20.2	13.4	0.00297	0.02022
0.07	0.350	132	30.1	20.6	0.00232	0.02119
0.08	0.322	132	48.6	33.9	0.00165	0.02408
0.09	0.300	139	92.3	65.5	0.000975	0.02610
0.1	0.280	146	166	120	0.000604	0.0275
0.2	0.280	156	219	158	0.000915	0.0552
0.4	0.280	167	270	195	0.00148	0.1112
0.6	0.280	176	321	232	0.00187	0.1662
0.8	0.280	176	321	232	0.00249	0.2216

Above the maximum, the latter effect is by far the predominant one. The application of Stokes' law in the manner explained above implies rather large mobilities and conductivities for the micelles. For instance, at $C = 0.07$, the concentration at which the conductivity goes through a minimum, the velocity of the average micelle is 3.1 times that of the simple anion and 0.19 times that of the hydrogen ion; its conductivity is 29.4 times that of the simple anion and 1.9 times that of the hydrogen ion. The largest average micelle, $H_{232}L_{331}$, has a velocity equal to 13 times that of the simple anion and 0.82 times that of the hydrogen ion; its conductivity is 1156 times that of the simple anion and 73 times that of the hydrogen ion.

It is interesting to note that the electric field at the surface of this largest micelle is only 1.9 times that at the surface of the simple anion, when both are assumed spherical. Actually, the field at the active end of the simple anion is much larger than for a hypothetical spherical ion and the true ratio of the fields is certainly much smaller than 1.9.

The above results would of course be modified to a certain extent if viscosity changes could be taken into account. Viscosities of laurylsulfonic acid solutions have been measured by Mrs. McBain (8) and are used in the next section of this paper in connection with diffusion data.

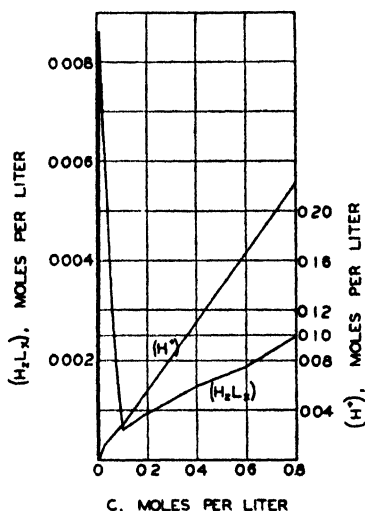


FIG. 3

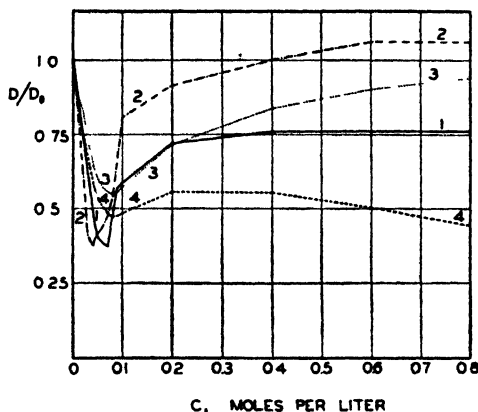


FIG. 4

FIG. 3. Variation with total concentration, C , of the concentrations of the average micelle and of the hydrogen ion in aqueous solutions of laurylsulfonic acid.

FIG. 4. Curve 1, experimental values of \bar{D}/D_0 ratios (integral values of diffusion coefficient); curve 2, calculated values of \bar{D}/D_0 ratios (differential values of diffusion coefficient); curve 3, calculated values of \bar{D}/D_0 ratios; curve 4, calculated values of \bar{D}/D_0 ratios tentatively corrected for viscosity.

Structural viscosity is probably predominant in the more concentrated solutions, and it is impossible to carry out viscosity corrections with any degree of certainty.

III. DIFFUSION COEFFICIENTS OF LAURYL-SULFONIC ACID IN AQUEOUS SOLUTION CALCULATED ON THE BASIS OF THE AVERAGE MICELLE. PREDICTION OF TRANSPORT NUMBERS

Integral diffusion coefficients of laurylsulfonic acid have been measured by Mrs. McBain (7). The ratios of the average diffusion coefficient \bar{D} to the limiting value D_0 for infinite dilution are given in table 2 (column 2)

and are plotted on figure 4 (curve 1). The theoretical value of D_0 is given by the Nernst formula:

$$D_0 = 2RT \frac{u_+^0 u_-^0}{u_+^0 + u_-^0} \quad (18)$$

in which u_+^0 and u_-^0 are the mobilities of the simple ions at infinite dilution. With u_+^0 equal to 350 and u_-^0 to 22, we find, at 25°C., $D_0 = 0.952$

TABLE 2

Differential and integral diffusion coefficients of laurysulfonic acid in aqueous solution calculated on the basis of the average micelle

c	B/D_0 (EXPERIMENTAL)	D/D_0 (CALCULATED)	B/D_0 (CALCULATED)	B/D_0 (CORRECTED FOR VISCOSITY)
0	1.000	1.000	1.000	1.000
0.005	0.919	0.855	0.927	0.907
0.01	0.872	0.866	0.893	0.865
0.02	0.735	0.639	0.823	0.760
0.03	0.625	0.414	0.724	0.664
0.04	0.473	0.376	0.642	0.581
0.05	0.402	0.423	0.593	0.531
0.06	0.383	0.445	0.566	0.502
0.07	0.373	0.481	0.552	0.484
0.08	0.499	0.547	0.547	0.475
0.09	0.567	0.691	0.555	0.477
0.1	0.586	0.813	0.575	0.485
0.2	0.720	0.915	0.719	0.556
0.4	0.762	1.001	0.839	0.554
0.6	0.762	1.064	0.903	0.504
0.8	0.762	1.064	0.943	0.446

cm.² per day. For an unsymmetrical salt dissociating into ν_+ positive and ν_- negative ions, we have

$$D = (\nu_+ + \nu_-)RT \frac{u_+ u_-}{u_+ + u_-} \quad (19)$$

In our case we have, for each molecule of acid, $(x - z)/x$ hydrogen ions and $1/x$ micelles. The solution being assumed ideal in terms of the average micelle, we calculate the differential diffusion coefficient D at each concentration by means of the Nernst formula or the ratio D/D_0 by means of the following formula deduced from formulas 19, 18, and 9:

$$\frac{D}{D_0} = \frac{(x - z + 1)(x - z)}{2x^{4/3}} \cdot \frac{1.063}{1 + 0.063 \frac{x - z}{x^{1/3}}} \quad (20)$$

The results are reported in table 2 (column 3) and plotted on figure 4 (curve 2). In column 4 we give the corresponding integral values, which are directly comparable with the experimental results given in column 2 (see also curve 3 of figure 4). In the last column of table 2 (and also in figure 4, curve 4) we give \bar{D}/D_0 ratios tentatively corrected for viscosity, according to the formula proposed by Gordon (1) and Van Rysselberghe (17). The correction is applied to the differential values of column 3 and the new values of the ratios D/D_0 are then transformed into integral values \bar{D}/D_0 . We have

$$\left(\frac{D}{D_0}\right)_{\text{visc.}} = \frac{1}{\eta} \cdot \frac{D}{D_0} \quad \left(\frac{\bar{D}}{D_0}\right)_{\text{visc.}} = \frac{1}{C} \int_0^C \left(\frac{D}{D_0}\right)_{\text{visc.}} dC \quad (21)$$

in which η is the viscosity of the solution referred to pure water. The viscosities used in our calculations have been measured by Mrs. McBain (8). It is indeed remarkable that, as shown in figure 4, our calculated values, both without and with viscosity correction, exhibit a minimum at practically the same concentration as the experimental curve. At concentrations higher than 0.1 the viscosity increases very rapidly and may be of a structural type, which renders the correction applied to diffusion coefficients uncertain. In fact we do not attach much weight to the viscosity correction as a whole in the present case, since the model was established by means of calculations on conductivities in which the change of viscosity with concentration was neglected. An interesting application of diffusion data to the determination of the size of micelles was recently published by Hartley and Runnicles (4).²

It is also possible to predict, on the basis of our model, the transport numbers of hydrogen and of the simple laurylsulfonate radical. The formulas are

$$\begin{aligned} T_- &= \frac{(H_s L_s) \cdot \frac{x-z}{x^{1/3}} \cdot x \cdot 22}{(H^+) \cdot 350 - (H_s L_s) \cdot \frac{x-z}{x^{1/3}} \cdot z \cdot 22 + (H_s L_s) \cdot \frac{x-z}{x^{1/3}} \cdot x \cdot 22} \\ &= \frac{x}{15.9x^{1/3} + x - z} \end{aligned} \quad (22)$$

$$T_+ = 1 - T_- = \frac{15.9x^{1/3} - z}{15.9x^{1/3} + x - z} \quad (23)$$

² Note added in proof: While this paper was in the process of publication, G. S. Hartley (Trans. Faraday Soc. 35, 1109 (1939)) has given a qualitative interpretation of the minimum in Mrs. McBain's diffusion curves on the basis of an ionic micelle of constant size and charge in equilibrium with the simple ions.

With the values of x and z reported in table 1 we find $T_- = 0.060$ and $T_+ = 0.940$ at $C = 0.005$, and $T_- = 1.620$ and $T_+ = -0.620$ at $C = 0.8$, the transport number of hydrogen becoming negative between the concentrations 0.09 and 0.1. Further refinements in our calculations, such as the viscosity corrections mentioned above, might alter these predictions considerably.

IV. AVERAGE, IONIC, AND NEUTRAL MICELLES

It would be highly interesting and useful to have some precise information as to the actual micelles and ions of which our H_sL_x micelle is the average. McBain (13) has been of the opinion that an ionic micelle of high mobility and high conductivity, and a neutral micelle, or at least a practically neutral one of low conductivity³, are necessary in order to explain all the properties of soap solutions, and hence those of an electrolyte like laurylsulfonic acid. This point of view has been criticized by Hartley (3) and discussed by Tartar and his collaborators (15, 18, 19). The distribution of our average micelle among two or more types must, of necessity, be based on some rather arbitrary assumptions. In order to clear the ground we shall first show that the decomposition of H_sL_x into an ionic micelle, L_n , and an exactly neutral one, H_mL_m , or into H_sL_s and H_mL_m , is incompatible with Stokes' law as applied above.

1. Decomposition of H_sL_x into $L_n + H_mL_m$:

The electroneutrality condition gives

$$n(L_n) = x - z(H_sL_x) \quad (24)$$

Since

$$(L_n) + (H_mL_m) = (H_sL_x) = iC - (H^+) \quad (25)$$

we have, obviously, from equations 24 and 25:

$$(L_n) < (H_sL_x) \text{ and } n > x - z \quad (26)$$

The conductivity would require

$$n^{5/3}(L_n) = x^{-1/3}(x - z)^2(H_sL_x) \quad (27)$$

Dividing equation 27 by equation 24 we get

$$n^{2/3} = x^{-1/3}(x - z) = x^{2/3}\left(1 - \frac{z}{x}\right) \quad (28)$$

³ Estimates of this conductivity can be deduced from Mrs. McBain's work on the migration and electrokinetic properties of soap solutions and soap curds (J. Phys. Chem. **28**, 673 (1924); Trans. Faraday Soc. **31**, 153 (1935)).

The second inequality (formula 26) gives, since both n and $x - z$ are larger than unity,

$$n^{2/3} > (x - z)^{2/3} \quad \text{or} \quad n^{2/3} > x^{2/3} \left(1 - \frac{z}{x}\right)^{2/3} \quad (29)$$

But, since $1 - \frac{z}{x}$ is smaller than unity,

$$\left(1 - \frac{z}{x}\right)^{2/3} > 1 - \frac{z}{x} \quad (30)$$

which shows that formula 29 is incompatible with formula 28.

2. Decomposition of H_sL_z into $H_aL_b + H_mL_m$:

The electroneutrality condition gives

$$(b - a)(H_aL_b) = (x - z)(H_sL_z) \quad (31)$$

Since

$$(H_aL_b) + (H_mL_m) = (H_sL_z) = iC - (H^+) \quad (32)$$

we have, obviously, from equations 31 and 32:

$$(H_aL_b) < (H_sL_z) \quad \text{and} \quad b - a > x - z \quad (33)$$

The conductivity would require

$$b^{-1/3}(b - a) = x^{-1/3}(x - z) \quad (34)$$

Dividing equation 34 by equation 31 we get

$$b^{-1/3}(b - a)^2(H_aL_b) = x^{-1/3}(x - z)^2(H_sL_z) \quad (35)$$

and, hence, since $b - a > x - z$,

$$b^{-1/3} < x^{-1/3} \quad \text{or} \quad b > x \quad (36)$$

On the other hand we have

$$(H^+) = C \frac{x - z}{x} = [C - m(H_mL_m)] \frac{b - a}{b} \quad (37)$$

which requires

$$\frac{b - a}{b} > \frac{x - z}{x} \quad (38)$$

Combining expressions 35 and 38 we find

$$b^{2/3} < x^{2/3} \quad \text{or} \quad b < x \quad (39)$$

which is incompatible with expression 36.

It is quite possible, however, that neutral molecules and aggregates are present in these solutions, as is suggested by the variation of the apparent degree of dissociation, α (formula 17 and figure 2). If one gives up the condition that the conductivity must be accounted for by Stokes' law applied to the ionic micelle alone (formulas 27 and 34) and assumes that this law should be applied only to the average micelle, as has been done above, it is possible to decompose $(H_n L_x)$ into (L_n) and $(H_m L_m)$, but such a decomposition could be done in an infinite number of ways. One might, for example, suppose that n and m are equal and hence that the ionic and the neutral micelle have the same size at each concentration, although this particular assumption is not in agreement with the results of ultrafiltration. This would lead immediately to the following conditions:

$$n(H_n L_n) = z(H_s L_x) \quad n(L_n) = (x - z)(H_s L_x) \quad (40)$$

and hence to

$$(H_n L_n) = \frac{z}{x} (H_s L_x), \quad (L_n) = \frac{x - z}{z} (H_s L_x), \quad n = x \quad (41)$$

We have calculated these concentrations $(H_n L_n)$ and (L_n) from the data of table 1 and have tried to deduce from them the equilibrium constants of the successive equilibria

$$(L_2) = K(L)(L), \quad (L_3) = K(L_2)(L) = K^2(L)^3, \dots \dots \dots (42)$$

$$(H_2 L_2) = K'(HL)^2, \quad (H_3 L_3) = K'(H_2 L_2)(HL) = K'^2(HL)^3, \dots (43)$$

according to the theory suggested by Meyer and van der Wyk (14) applied to both the ionic and neutral polymers, assuming that the successive constants have the same value (K and K' , respectively) in each of the two series of equilibria. The constants thus obtained turn out to be fairly "constant," at least in the more concentrated solutions, and are very large. They correspond to distribution curves $[(L_n)$ and $(H_n L_n)$ plotted against n] with flat maxima. This question of the actual distribution of the average micelle requires much more extensive examination and we hope to come back to it in later communications.

V. SUMMARY

1. Freezing point and conductivity data for aqueous solutions of lauryl-sulfonic acid are interpreted on the basis of an "average inclusive micelle," whose size and charge vary with concentration and in terms of which the solution is considered as ideal, assuming the sole constituents of the solution at all concentrations to be free hydrogen ion and this "average micelle."

2. The Nernst formula for the diffusion coefficient of an unsymmetrical

electrolyte is applied to this average micelle, and the main features of the experimental diffusion curve are thereby reproduced. Some predictions are made as to the variation of transport numbers with concentration.

3. The possibility of decomposing the average micelle into ionic and neutral micelles is discussed.

It is a pleasure to acknowledge here the valuable suggestions of Professor McBain and his interest in our work.

REFERENCES

- (1) GORDON, A. R.: *J. Chem. Phys.* **5**, 522 (1937); **7**, 89 (1939).
- (2) HARTLEY, G. S.: *Trans. Faraday Soc.* **30**, 444 (1934).
- (3) HARTLEY, G. S.: *Aqueous Solutions of Paraffin-Chain Salts.—A Study in Micelle Formation. Actualités Scientifiques et Industrielles*, No. 387, Paris, Hermann and Co. (1936).
- (4) HARTLEY, G. S., AND RUNNICLES, D. F.: *Proc. Roy. Soc. (London)* **A168**, 420 (1938).
- (5) LANGMUIR, I.: *J. Chem. Phys.* **6**, 873 (1938).
- (6) LEVINE, S.: *Proc. Roy. Soc. (London)* **A170**, 145, 165 (1939).
- (7) MCBAIN, E. L.: *Proc. Roy. Soc. (London)* **A170**, 415 (1939).
- (8) MCBAIN, E. L., DYE, W. B., AND JOHNSTON, S. A.: *J. Am. Chem. Soc.*, in press.
- (9) MCBAIN, J. W.: *Trans. Faraday Soc.* **9**, 99 (1913).
- (10) MCBAIN, J. W., AND BETZ, M. D.: *J. Am. Chem. Soc.* **57**, 1905 (1935).
- (11) MCBAIN, J. W., AND BETZ, M. D.: *J. Am. Chem. Soc.* **57**, 1909 (1935).
- (12) MCBAIN, J. W., AND BETZ, M. D.: *J. Am. Chem. Soc.* **57**, 1913 (1935).
- (13) MCBAIN, J. W., AND SALMON, C. S.: *Proc. Roy. Soc. (London)* **A97**, 44 (1920).
- (14) MEYER, K. H., AND VAN DER WYK, A.: *Helv. Chim. Acta* **20**, 1321 (1937).
- (15) TARTAR, H. V., AND WRIGHT, K. A.: *J. Am. Chem. Soc.* **61**, 539 (1939).
- (16) VAN RYSSELBERGHE, P.: *J. Phys. Chem.* **38**, 645 (1934).
- (17) VAN RYSSELBERGHE, P.: *J. Am. Chem. Soc.* **60**, 2326 (1938).
- (18) WRIGHT, K. A., ABBOTT, A. D., SIVERTZ, V., AND TARTAR, H. V.: *J. Am. Chem. Soc.* **61**, 549 (1939).
- (19) WRIGHT, K. A., AND TARTAR, H. V.: *J. Am. Chem. Soc.* **61**, 544 (1939).

MOLECULAR WEIGHT OF SOL AND GEL IN CRUDE HEVEA RUBBER¹

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In a previous article (1) a simple procedure for determining the sol rubber content of Hevea latex and crude rubber was described. This method is based on the fact that the sol rubber diffuses into a solvent, such as petroleum ether or hexane, in which the rubber is placed. The solution can be readily decanted from the highly swollen gel, so by periodic change to fresh solvent it is possible to fractionate the sol content into numerous fractions, depending upon their relative solubility and rate of diffusion into the solvent.

In the present investigation the molecular weights of sol rubber fractions in hexane were determined by the well-known viscosity method developed by Staudinger (2). This method has been proven satisfactory in the case of numerous polymeric substances in the range of molecular weights capable of being checked by standard methods. Several investigators, however, have questioned on theoretical grounds its absolute accuracy for extremely high polymers such as natural rubber. It can be said in support of Staudinger's work that the average molecular weight of crude rubber determined by the osmotic pressure and ultracentrifuge methods is of the same order as shown by the viscosity method. In spite of the lack of proof that the viscosity method gives the true molecular weight of extremely high polymeric substances, it is of utmost value in providing a simple procedure for comparative purposes. The work on the viscosity molecular weight of crude rubber has so far been confined to the determination of the viscosity of very dilute dispersions of whole crepe or smoked sheet in benzene, toluene, or tetralin. These dispersions have been prepared by first allowing the rubber to imbibe the solvents and swell, followed by shaking the liquid vigorously to break up the swollen gel and disperse it, while at the same time the sol portion has entered into solution. The refractive indices of these solvents are so close to that of rubber hydrocarbon that it is very difficult to determine when the dispersion is complete. Staudinger apparently has favored tetralin over other solvents, since it appears

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to disperse the gel more completely. It is very difficult to disperse completely the gel of high-quality plantation crude rubber in benzene or toluene in the absence of oxygen, and for this reason the use of these solvents is not advisable. The influence of the dispersed gel on the viscosity is likely to be a variable, depending upon the size of the gel aggregates and the amount present. On the other hand, some types of plantation crepes of high sol content will disperse readily in benzene.

It will be shown that the viscosity of dilute crude rubber dispersions in tetralin decreases rapidly in spite of the fact that care is taken to exclude oxygen. Tetralin is objectionable on account of its relatively high viscosity. It is likely to contain difficultly removable, chemically active substances which catalyze the oxidation breakdown of the rubber hydrocarbon, thereby reducing its molecular weight.

In the present work the gel rubber was completely excluded by employing the diffusion process of separating the sol from the gel and of separating the sol into fractions of increasing molecular weight and decreasing solubility. Hexane was employed as the solvent on account of its complete inertness, non-polarity, ease of handling, and its ability to fractionate clearly the sol from the gel, leaving all solid non-hydrocarbon substances in the gel skeleton. The hexane solutions were perfectly clear, except for a faint opalescence due to the Tyndall effect of colloidal solutions.

PROCEDURE

An Ostwald viscosimeter placed in a water bath held at $25^{\circ}\text{C.} \pm 0.1^{\circ}$ was employed. Exactly 5 cc. of solution was pipetted into the viscosimeter for each determination. Great care was taken in cleaning the viscosimeter between runs and to avoid the entrance of fibers or dirt particles into the viscosimeter. The length of the capillary of the viscosimeter was 103.0 mm.; its bore was 0.066 to 0.067 mm. The times of flow in seconds at 25°C. for different liquids were as follows: distilled water, 95.2; *n*-hexane, 50.7; benzene, 72.7; tetralin, 215.4. The *n*-hexane is known as Skellysolve. It was obtained from the Skelly Oil Company and had a boiling range of 66° to 70°C.

A uniform sheet of R.C.M.A.² crepe was selected for the fractionating experiments, and adjacent sheets from the same bale were employed in the milling experiments. The apparatus and procedure employed in the extraction of the sol fractions by *n*-hexane was the same as that previously described by the authors (1). The concentration of sol in the hexane solutions was accurately determined by evaporating definite volumes to dryness to a constant weight of residue. Wherever necessary the acetone

² R.C.M.A. = Rubber Culture Maatschappij Amsterdam.

extract was made on the residue to determine the amount of "resin substances present." The concentrations of the solutions were adjusted to those required for the viscosity measurements by exactly controlled dilution with hexane.

Since the rate of diffusion of sol into hexane is most rapid for fractions having the lowest molecular weight, the time of extraction for each fraction was increased as fractionation proceeded. Care was taken to exclude light from the solutions, and air was displaced over the solutions with a stream of nitrogen. Viscosities were measured as soon as possible after decanting the solution from the swollen gel.

The average molecular weight was calculated by the use of the Staudinger formula

$$M = \frac{\eta_{sp}}{C \cdot 3 \times 10^{-4}}$$

where C is the base molal concentration, i.e., one mole is taken as 68 g. of the rubber hydrocarbon base unit (C_5H_8) per liter. The value 3×10^{-4} is Staudinger's K_m constant, which varies with the material and in this case is the value found when equating the viscosity molecular weight of low-molecular broken-down rubber with the molecular weight as determined by the freezing point method. The average molecular weight was also calculated by the formula based on the Arrhenius equation

$$\frac{\log \eta_r}{C} = Kc$$

In this case

$$M' = \frac{\log_{10} \eta_r \cdot 10^4}{C}$$

Excellent agreement in duplicate viscosity runs was obtained using hexane solutions. In the more dilute solutions, where η_r was less than about 3, variations were not over ± 0.1 sec. With the more viscous solutions, which had a value for η_r of 3 or more, the duplicate values were not so close but were very satisfactory.

MOLECULAR WEIGHT RANGE OF SOL IN CREPE

The results shown in tables 1 and 2 show that the particular lot of R.C.M.A. crepe studied contains sol rubber, which can be separated into fractions having an average molecular weight range of 78,000 to 213,000. The presence of acetone-soluble substances apparently had little effect on the results. If M and M' are plotted against relative viscosity, it was found that the curves crossed in every case at η_r varying between 1.66 and 1.70. The molecular weight values selected, given in parentheses, were those corresponding to these relative viscosities. When the relative

viscosity of the solution is 1.6615, M becomes equal to M' , as is seen by inserting the log of this value and the value of 0.6615 for the specific

TABLE 1

Viscosity molecular weight of hexane-soluble fractions from whole unmilled R.C.M.A. crepe

BASE MOLARITY <i>C</i>	RATE OF FLOW	η	$M = \frac{\eta_{sp}}{C \cdot 8 \times 10^{-4}}$	MOLECULAR WEIGHT VALUES SELECTED	$M' = \frac{\log \eta_{sp} \cdot 10^4}{C}$
2.5-hr. extract (12.7 per cent)					
	<i>seconds</i>				
0.0158	68.2	1.345	72,700	(80,000)	81,500
0.0211	75.2	1.483	76,300		81,100
0.0316	90.4	1.783	82,500		79,500
0.0632	152.7	3.011	106,000		75,500
1-day extract (30.3 per cent)					
0.00908	67.7	1.335	123,000	(138,000)	138,000
0.0109	71.9	1.418	128,000		139,000
0.0136	78.3	1.544	133,000		139,000
0.0182	89.7	1.769	141,000		136,000
0.0273	116.8	2.303	159,000		133,000
0.0545	240.2	4.737	229,000		124,000
8-day extract (44.2 per cent)					
0.00515	63.1	1.244	158,000	(187,000)	184,000
0.00687	68.0	1.341	165,000		185,000
0.0103	79.2	1.562	182,000		188,000
0.0206	120.6	2.378	223,000		183,000
0.0412	262.2	5.171	337,000		173,000
13-day extract (49.0 per cent)					
0.00228	56.8	1.120	175,000	(210,000)	216,000
0.00343	59.6	1.176	171,000		205,000
0.00457	63.7	1.256	187,000		217,000
0.00685	70.5	1.391	190,000		209,000
0.0137	98.3	1.939	229,000		210,000
21-day extract (53.0 per cent)					
0.00900	76.3	1.505	187,000	(197,000)	197,000
0.0101	80.0	1.578	191,000		196,000
0.0135	93.6	1.846	209,000		197,000

viscosity in the two equations. It will be noted that the average molecular weight calculated by the Staudinger equation showed a greater deviation with change in concentration than in the case of the values based on the

TABLE 2

Viscosity molecular weight of hexane-soluble fractions of unmilled acetone-extracted R.C.M.A. crepe

BASE MOLARITY C	RATE OF FLOW	η_r	$M = \frac{\eta_{sp}}{C \cdot 8 \times 10^{-4}}$	MOLECULAR WEIGHT VALUES SELECTED	$M' = \frac{\log \eta_r \cdot 10^4}{C}$
1-hr. extract (4.4 per cent)					
	<i>seconds</i>				
0.0140	65.6	1.293	69,700	(78,000)	82,900
0.0210	74.8	1.475	75,400		80,400
0.0280	84.4	1.664	79,000		79,000
0.0420	107.5	2.120	89,000		77,700
0.0840	205.4	4.051	121,000		72,300
2-hr. extract (12.9 per cent)					
0.0100	66.1	1.303	101,000	(115,000)	115,000
0.0150	76.3	1.504	112,000		118,000
0.0300	110.9	2.187	132,000		113,000
0.0600	211.0	4.161	176,000		103,000
4-hr. extract (18.6 per cent)					
0.0105	67.7	1.335	106,000	(115,000)	120,000
0.0157	75.5	1.489	104,000		110,000
0.0315	115.5	2.278	135,000		114,000
0.0630	232.4	4.583	190,000		105,000
7-hr. extract (23.4 per cent)					
0.00866	66.6	1.313	121,000	(134,000)	137,000
0.0130	76.2	1.503	129,000		136,000
0.0260	110.8	2.190	153,000		131,000
0.0520	220.2	4.343	214,000		123,000
2-day extract (30.0 per cent)					
0.00525	62.7	1.236	156,000	(172,000)	175,000
0.0105	76.9	1.517	164,000		172,000
0.0140	88.2	1.740	176,000		172,000
0.0210	114.8	2.264	201,000		169,000
0.0840	849.0	16.746	625,000		146,000
4-day extract (37.0 per cent)					
0.00570	64.4	1.270	158,000	(179,000)	182,000
0.00718	68.4	1.349	162,000		181,000
0.00957	75.4	1.487	170,000		180,000
0.0144	91.4	1.803	186,000		178,000
0.0287	160.1	3.156	250,000		174,000
0.0574	—	—	—		—

TABLE 2—*Concluded*

BASE MOLALITY <i>C</i>	RATE OF FLOW	η	$M = \frac{\eta_{sp}}{C \times 10^{-4}}$	MOLECULAR WEIGHT VALUES SELECTED	$M' = \frac{\log \eta_{sp} \cdot 10^4}{C}$
9-day extract (42.4 per cent)					
	<i>seconds</i>				
0.00335	59.1	1.166	158,000	(197,000)	199,000
0.00503	63.8	1.258	171,000		198,000
0.00719	70.6	1.393	182,000		200,000
0.0126	89.7	1.769	203,000		197,000
0.0168	107.5	2.120	222,000		194,000
—	—	—	—		—
14-day extract (46.4 per cent)					
0.00554	65.7	1.296	178,000	(206,000)	203,000
0.00776	73.3	1.446	192,000		206,000
0.0129	93.3	1.840	217,000		205,000
0.0194	125.4	2.474	253,000		203,000
16-day extract (47.8 per cent)					
0.00953	80.4	1.586	205,000	(210,000)	211,000
0.0143	100.8	1.988	230,000		209,000
20-day extract (49.0 per cent)					
0.00870	75.9	1.497	190,000	(201,000)	201,000
0.0116	86.7	1.710	204,000		201,000
30-day extract (50.3 per cent)					
0.00942	79.3	1.564	200,000	(207,000)	206,000
0.01259	92.2	1.820	219,000		208,000
48-day extract (52.4 per cent)					
0.0115	88.8	1.751	218,000	(213,000)	212,000
0.0172	118.0	2.327	257,000		213,000

Arrhenius equation. In other words, the deviation of η_{sp}/C from constancy at various concentrations was much greater than $\log_{10} \eta_r/C$, as is shown in figure 1, in which the data from the 4-day extract in table 2 were used. This deviation is even more apparent at higher concentrations,—for example, in the 2-day extract in table 2 at 0.0210 and 0.0840 molarity. η_{sp}/C increases from 29 to 271, while $\log_{10} \eta_r/C$ decreases from 16.9 to 14.6. Many additional comparisons leading to the same conclusion can be made from the tabulated data. It should be noted that the lowest concen-

trations were considerably below those employed by Staudinger and others in determining the viscosity molecular weight of crude rubber.

Table 3 gives a summary of the molecular weight data in tables 1 and 2 and includes the weighted average molecular weights based on each fraction. It has been assumed in this case that the gel has a molecular weight equal to that of the extract giving the highest molecular weight. The authors believe, however, that the molecular weight of the gel is higher than this value.

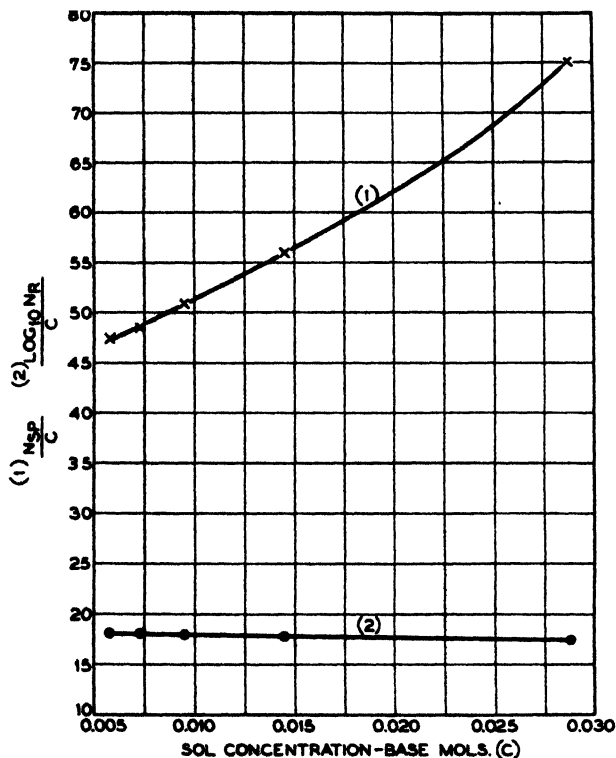


FIG. 1. Relation between viscosity and concentration of solutions of sol rubber in hexane.

The molecular weight distribution will depend upon the particular rubber under test and upon the fractionation procedure. For example, when 5 g. of finely cut, acetone-extracted, yellow crepe of high sol content was placed in 250 cc. of hexane, 3.0 per cent sol was extracted in 1 hr. at room temperature. This sol was found to have a molecular weight of 63,000. When Brazilian fine para of low sol content was similarly treated for 2 hr., 1.7 per cent sol of a molecular weight of 64,000 diffused into the hexane.

TABLE 3

Summary of molecular weight data on hexane-soluble fractions of crepe rubber

FRACTION NO.	EXTRACTION PERIOD	EXTRACT	MOLECULAR WEIGHT CALCULATED AT η OF 1.7
R.C.M.A. crepe			
	hours	per cent	
1	2.5	12.7	80,000
2	21.5	17.6	188,000
3	168.0	13.9	187,000
4	120.0	4.8	210,000
5	192.0	4.0	197,000
Total extract..... .53.00			
Residue..... .47.0 >210,000			
Weighted average molecular weight of extract.....148,000			
Weighted average molecular weight of whole rubber*...177,000			

R.M.C.A. crepe (acetone-extracted)

	hours	per cent	
1	1	4.4	78,000
2	1	8.5	115,000
3	2	5.7	115,000
4	3	4.8	134,000
5	41	6.6	172,000
6	48	7.0	179,000
7	120	5.4	197,000
8	120	4.0	206,000
9	48	1.4	210,000
10	96	1.2	201,000
11	240	1.3	207,000
12	432	2.1	212,000
Total extract..... .52.4			
Residue..... .47.6 >212,000			
Weighted average molecular weight of extract.....156,000			
Weighted average molecular weight of whole rubber*...192,000			

* Using molecular weight of last extract for that of residual gel; proteins and resins ignored.

VISCOSITY OF MILLED CREPE IN HEXANE, BENZENE, AND TETRALIN

Since the Staudinger K_m constant of 3×10^{-4} was established on broken-down rubber in benzene and tetralin, a comparison of the viscosities of a sample of milled crepe was made in these solvents with the viscosity of the same rubber in *n*-hexane. These results are shown in table 4. It was felt that the agreement of the results in hexane with those in the other solvents was sufficiently close to justify employing the Staudinger K_m constant in calculating the molecular weight from the viscosity data of the hexane

solutions. The average molecular weight calculated from the hexane solutions was about 10 per cent lower than that given by the benzene and tetralin solutions. Further work would be required to determine the cause of this difference.

Benzene and tetralin are satisfactory solvents for viscosity molecular weight studies of well-masticated rubber, since this rubber is completely soluble in these solvents and resists further oxidative breakdown in tetralin on account of having been already oxidized during mastication.

TABLE 4

Viscosity molecular weight of masticated crepe in different solvents*

BASE MOLARITY <i>C</i>	RATE OF FLOW	η_r	$M = \frac{\eta_{sp}}{C \cdot 3 \times 10^{-4}}$	MOLECULAR WEIGHT VALUES SELECTED	$M' = \frac{\log_{10} \eta_r \cdot 10^4}{C}$
Hexane, 50.7 sec.					
	<i>seconds</i>				
0.0500	71.5	1.410	27,300	(30,000)	29,800
0.0625	77.8	1.535	28,500		29,800
0.0833	90.2	1.779	31,200		30,000
0.2500	240.0	4.779	49,700		27,000
Benzene, 72.7 sec.					
0.0500	107.4	1.477	31,800	(33,000)	33,900
0.0625	117.9	1.621	33,000		33,600
0.0833	137.0	1.884	35,400		33,000
0.2500	369.0	5.075	54,300		28,200
Tetralin, 215.4 sec.					
0.0500	320.2	1.486	32,400	(33,000)	34,400
0.0625	348.0	1.615	32,800		33,300
0.0833	401.4	1.864	34,600		31,300
0.2500	1059.0	4.916	52,200		27,600

* 300-g. batch of R.C.M.A. crepe broken down for 25 min. on cool laboratory mill rolls with separation of 0.035 in.

MOLECULAR WEIGHT OF MILLED CREPE FRACTIONS

Fractionation of milled crepe was carried out by the procedure already referred to (1). The molecular weight data on these fractions are given in table 5. These data show that a thorough breakdown on the mill results in a product which has a rather narrow range of molecular weight. This might be expected, since the highest polymers offer the greatest frictional resistance and would be the most rapidly broken down. The low polymers, on the other hand, would constitute the plastic phase. Data of this kind are very valuable in the study of rubber breakdown under various conditions. If the same rubber is broken down under the same

milling conditions at higher temperatures, the range of molecular weights is greater and the average of the whole milled rubber is higher. These data are given in table 6 and explain why it is possible as a rule to obtain with hot milled rubber vulcanizates superior to those obtained with cold milling when other conditions are equal. The reduced breakdown at

TABLE 5
*Viscosity molecular weight of hexane-soluble fractions of milled crepe**

BASE MOLARITY <i>C</i>	RATE OF FLOW† <i>t_{sp}</i>	η_r	$M = \frac{\eta_{sp}}{C \cdot 8 \times 10^{-4}}$	MOLECULAR WEIGHT VALUES SELECTED	$M' = \frac{\log_{10} \eta_r \cdot 10^4}{C}$
0.5-hr. extract (1.6 per cent)					
0.00588	seconds 52.3	1.032	18,100		23,300
2.5-hr. extract (7.6 per cent)					
0.00690	53.2	1.049	23,700		30,110
0.0103	54.3	1.071	23,000		28,900
0.0207	58.2	1.147	23,700		28,700
7-hr. extract (36.5 per cent)					
0.0212	60.8	1.200	31,400		37,300
0.0425	73.7	1.453	35,500	(37,000)	38,200
0.0850	105.5	2.080	42,300		36,200
1-day extract (83.7 per cent)					
0.0233	62.3	1.228	32,600		38,300
0.0350	70.0	1.380	36,200	(39,000)	40,000
0.0700	95.0	1.874	41,600		39,000
0.1400	167.0	3.294	54,600		37,000
R.C.M.A. broken-down (whole rubber)					
0.0375	70.0	1.380	37,000		37,300
0.0502	77.9	1.536	35,600	(39,000)	37,100
0.0750	95.3	1.880	39,200		36,500
0.301	449.4	8.864	87,000		31,400

* 300-g. batch of R.C.M.A. crepe broken down for 15 min. on cool laboratory mill-rolls with separation of 0.035 in.

† Hexane, 50.7 sec.

96°C. as compared with 35°C. is believed to be due mainly to lower frictional forces. A different type of breakdown occurs at 142°C. Considerable fumes are given off and the rubber becomes reddish brown in color. Figure 2 shows the relative rates of hexane extraction of the hot and cool milled rubber under conditions already described (1).

TABLE 6

*Effect of milling temperature on molecular weight of hexane fractions of masticated crepe**

EXTRACTION PERIOD	EXTRACT	BASE MOLARITY	η_r	M'
I. Average mill roll temperature = 35°C.				
Hours	per cent			
3	17.6	0.0725	1.751	33,500
7	55.0	0.0684	1.848	39,000
24	23.0	0.0690	1.830	38,000
II. Average mill roll temperature = 96°C.				
3	8.4	0.0475	1.848	56,100
7	9.1	0.0325	1.696	70,600
24	30.2	0.0311	1.692	73,400
48	13.3	0.0391	1.968	75,200
144	29.6	0.0356	1.915	79,000
168	7.5	0.0212	1.460	77,500
III. Average mill roll temperature = 142°C.				
3	31.4	0.0480	1.927	59,400
7	25.9	0.0390	1.799	65,400
24	18.5	0.0376	1.744	64,300
48	6.5	0.0200	1.375	69,200
144	3.2	0.0116	1.212	63,000
Residue (gel)	14.5			

* 300 g. of R.C.M.A. crepe broken down for 15 min. on laboratory mill with roll opening of 0.089 cm.:

	I	II	III
Initial roll temperature, °C.	32	99	138
Final roll temperature, °C.	38	93	146
Final rubber temperature, °C.	43	90	140
Williams plasticity after standing 3 days, mm. ...	1.90	4.37	3.81

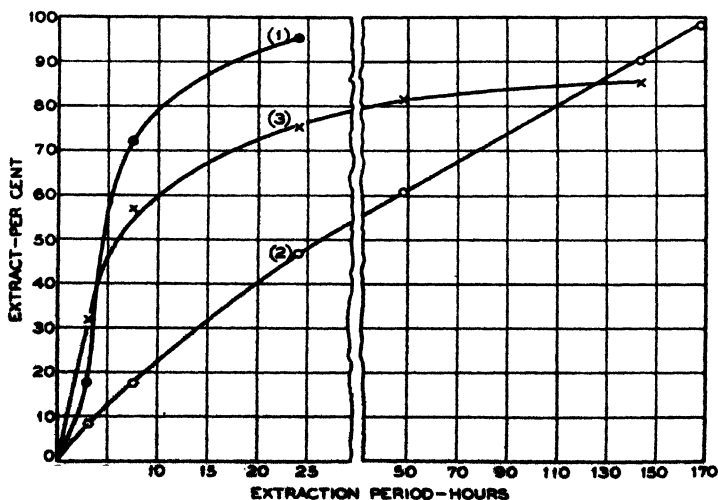


FIG. 2. Extraction of sol rubber in milled crepe: (1) milled at 35°C.; (2) milled at 96°C.; (3) milled at 142°C.

STABILITY OF RUBBER IN HEXANE AND TETRALIN

Hexane solutions of sol rubber showed relatively little change in viscosity on standing, as compared with crude rubber dispersed in tetralin. Changes in hexane solutions are shown in table 7. In these experiments the air above the solutions was not displaced with nitrogen, since this would remove hexane and change the concentration. The solutions were exposed to diffused light in tightly stoppered flasks. It is to be noted that

TABLE 7
Change in viscosity of hexane solutions of rubber on standing

CONCENTRATION BASE MOLARITY <i>C</i>	TIME OF FLOW	TIME OF STANDING	DIFFERENCE IN FLOW TIME
	<i>seconds</i>	<i>hours</i>	<i>seconds</i>
0.0632	152.7*		
0.0632	152.5	20	0.2
0.0632	150.6	96	2.1
0.0545	240.2*		
0.0545	235.7	72	4.5
0.0136	78.3*		
0.0136	77.9	72	0.4
0.0136	77.1	456	1.1
0.0140	88.2*		
0.0140	86.7	360	1.5
0.0105	76.9*		
0.0105	76.0	96	0.9
0.00228	56.8*		
	56.5	120	0.3
0.0115	88.8*		
0.0115	88.8	24	0.0

* Original value.

the maximum change in the relative viscosity of any of these solutions after long standing is less than 2 per cent. Since the air was displaced from over the hexane during the extraction periods and the solution was protected from light, it is believed that changes in viscosity during extraction were not significant.

In the case of tetralin two separate dispersions were prepared from unmilled R.C.M.A. crepe to yield a base molal concentration of 0.025. In the case of one solution the rubber was swelled for 72 hr. and then

shaken. In the case of the second solution the rubber was swelled in tetralin overnight and then frequently shaken during a 2-hr. period to disperse the swollen gel particles. In each case the first viscosity reading was made a few minutes after the final shaking and the change was then noted on repeated measurements at short intervals for longer periods. The results of changes in viscosity of the first solution are shown in table 8. These results indicate that tetralin is entirely unsuited to determinations of the molecular weight of crude rubber. The molecular weights calculated from the first viscosity measurements made on these solutions are as follows: $M = 185,000$ and $182,000$; $M' = 151,000$ and $150,000$. However, the rapid decrease in viscosity of the first solution gives values for M of $94,000$ and M' of $93,000$ after standing 24.5 hr. The rubber macro-

TABLE 8
Change in viscosity of 0.17 per cent crepe in tetralin

TIME OF STANDING	RATE OF FLOW	DIFFERENCE FROM ORIGINAL VALUE
	<i>seconds</i>	<i>seconds</i>
Original	513.8	
10 min.	491.0	22.8
20 min.	465.6	48.2
30 min.	450.0	63.8
2 hr.	428.8	85.0
2 hr., 11 min.	418.8	95.0
4 hr.	406.0	107.8
5 hr.	401.8	112.0
23 hr.	374.4	139.4
24.5 hr.	367.7	146.1

molecule is very sensitive to oxidation. The nitrogen used in this case to remove the air above the solution was the same as used in the case of hexane solutions. It appears that the use of tetralin may require a complete removal of oxygen to prevent breakdown of the rubber; this is a condition difficult to realize. The large decrease of viscosity following repeated measurements was surprising and unexpected. This change may be due to a shearing effect on the dispersed gel in addition to an oxidation effect. The authors were unable to find this effect previously mentioned in the case of tetralin dispersions of crude rubber, although Staudinger (2) followed the viscosity changes of rubber in tetralin over long periods of time. Broken-down rubber in tetralin did not show these changes. Since broken-down rubber is already oxidized and is free from gel, it would be expected to resist further oxidation. It is concluded that the effects noted in the case of crude rubber in tetralin are due to the influence of the dispersed gel and to a rapid breakdown of the large rubber

molecules. Staudinger and Bondy (3) have already noted great reductions in the viscosity of high-molecular rubber in tetralin upon standing.

MOLECULAR WEIGHT OF GEL RUBBER

The hexane extraction of crepe was carried out for somewhat longer periods than are shown in tables 1 and 2. The rate of extraction steadily diminishes, as is shown in figure 3. Whether the added extract is due to sol rubber present originally or to an oxidative breakdown of the gel is not known. The authors (1) have already shown the ease of converting gel to sol by oxidation. Small amounts of oxygen present in the nitrogen might be sufficient to cause some gel-sol conversion. On the other hand, the steadily diminishing amount of extract indicates a very slow extraction

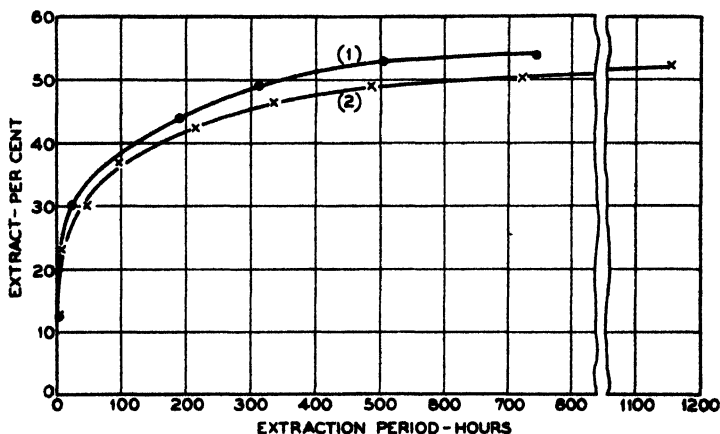


FIG. 3. Extraction of sol rubber from crepe with hexane: (1) whole R.C.M.A. crepe; (2) acetone-extracted R.C.M.A. crepe.

of the larger sol molecules. These results show that when the molecular weight exceeds 200,000 the solubility of rubber is very low. It appears that the molecular weight of gel rubber is greater than 210,000. It is impossible to do much more than speculate on the molecular weight range of gel rubber. However, if the molecular weight values of sol rubber fractions given in tables 1 and 2 are plotted as was done in figures 4 and 5, extrapolation of the curves indicates that the molecular weight of gel rubber may reach 300,000 or more.

The authors have already shown (1) that the rubber hydrocarbon in carefully prepared latex films is gel. Only about 3 per cent of sol rubber is present. This gel has not been passed through rolls, as is the case with the gel remaining in crude plantation rubber, so that one would expect it to be of a higher molecular order than the residual gel in crude rubber. Gel, of course, can exist in a range of molecular weights as well as sol.

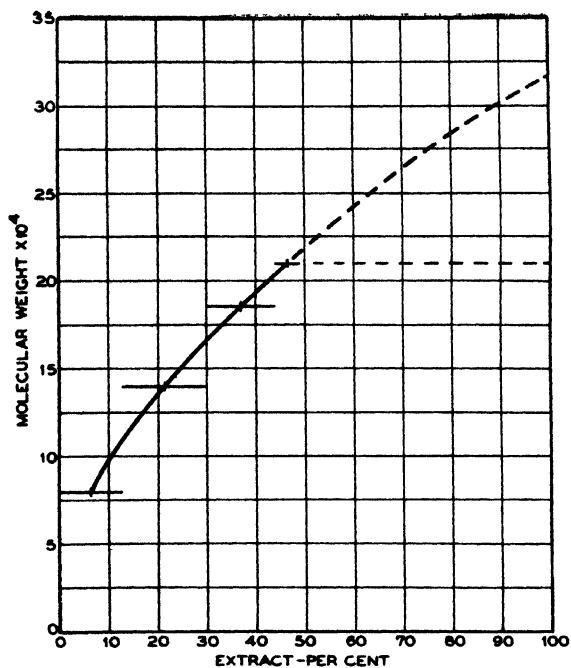


FIG. 4. Variation of molecular weight of successive fractions of sol rubber from crepe.

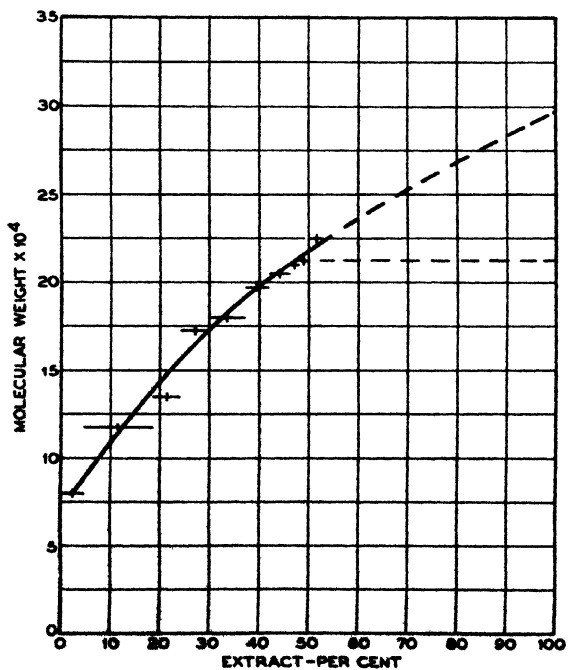


FIG. 5. Variation of molecular weight with successive fractions of sol rubber from acetone-extracted crepe.

Some evidence that indicates that latex contains gel of varying molecular complexity is given in figure 6. In this case it is shown that gel can be fractionated in hexane which contains 10 per cent of absolute alcohol and that the solubility diminishes as extraction proceeds. This evidence, together with that recently obtained (1) showing the high resistance of a portion of latex gel to oxidation, leads to the conclusion that the rubber gel in latex is present in variable molecular sizes.

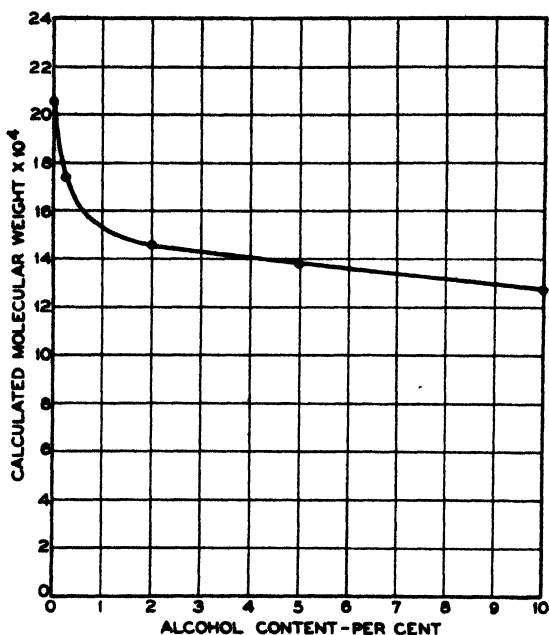


FIG. 6. Effect of adding alcohol to hexane solutions of sol rubber on the viscosity molecular weight.

EFFECT OF ABSOLUTE ETHYL ALCOHOL ON THE VISCOSITY OF HEXANE SOLUTIONS

The reduction in the viscosity of rubber cements by addition of polar solvents such as alcohols and ketones is well known. The effect of adding various quantities of absolute alcohol to the 14-day hexane fractions from the acetone-extracted R.C.M.A. shown in table 2 was studied. These results are given in table 9. The effect on the calculated molecular weight is shown in figure 6. In these experiments the viscosities were first measured in the absence of alcohol, then alcohol was added and the viscosities were measured immediately. It can therefore be stated that the decrease in relative viscosity due to the alcohol is immediate. These data show the importance of avoiding the presence of a polar solvent in viscosity molecular weight determinations.

EFFECT OF POLAR SOLVENTS ON GEL-SOL CONVERSION

The effect of adding 10 per cent of absolute ethyl alcohol on the extraction of dried latex film rubber was studied. The extraction was carried out by the procedure recently described by the authors (1). The results in figure 7 show the very great influence of alcohol on the peptizing of gel rubber. Experiments showed that when the hexane and alcohol were

TABLE 9

Effect of alcohol on viscosity of sol rubber in hexane

BASE MOLARITY <i>C</i>	RATE OF FLOW	η	$M = \frac{\eta_{sp}}{C \cdot 3 \times 10^{-4}}$	MOLECULAR WEIGHT VALUES SELECTED	$M' = \frac{\log_{10} \eta \cdot 10^4}{C}$
Hexane, 50.7 sec.					
	<i>seconds</i>				
0.00554	65.7	1.296	178,000	(206,000)	203,000
0.00776	73.3	1.446	192,000		206,000
0.0129	93.3	1.840	217,000		205,000
0.0194	125.4	2.474	253,000		203,000
99.75 per cent hexane + 0.25 per cent alcohol, 50.7 sec.					
0.0129	85.3	1.682	176,000	(175,000)	175,000
0.0194	110.2	2.173	202,000		174,000
98 per cent hexane + 2 per cent alcohol, 51.2 sec.					
0.00698	64.8	1.266	127,000		147,000
95 per cent hexane + 5 per cent alcohol, 51.6 sec.					
0.00698	64.9	1.258	123,000	(139,000)	143,000
0.0116	75.1	1.455	131,000		140,000
0.0175	89.6	1.736	140,000		137,000
90 per cent hexane + 10 per cent alcohol, 54.2 sec.					
0.00499	62.7	1.157	105,000	(127,000)	127,000
0.00698	66.3	1.223	107,000		125,000
0.0116	75.8	1.400	115,000		126,000
0.0175	90.4	1.668	127,000		127,000
0.0349	138.8	2.560	149,000		117,000

carefully removed by evaporation in nitrogen to avoid oxidation, the residual rubber was practically insoluble in hexane and behaved like gel.

Latex film rubber weighing 3.5 g., which had been completely extracted with hexane, was then extracted with 250 cc. of hexane containing 50 cc. of acetone for 3 days. At the end of this time the solution was decanted from the gel and the rubber precipitated from it by addition of acetone. This rubber was dried to constant weight in a stream of nitrogen

at room temperature. It amounted to 29.6 per cent of the original sample. The extraction was repeated with fresh solvent for 5 days, but no further rubber was extracted. It is apparent from this experiment that acetone is not as effective in peptizing gel as is ethyl alcohol; this might be expected, since alcohol is more polar than acetone.

The most logical explanation for the peptizing effect of polar solvents on rubber gel is that there is a large reduction in van der Waals forces resulting from the presence of polar groups. A change in the shape of the

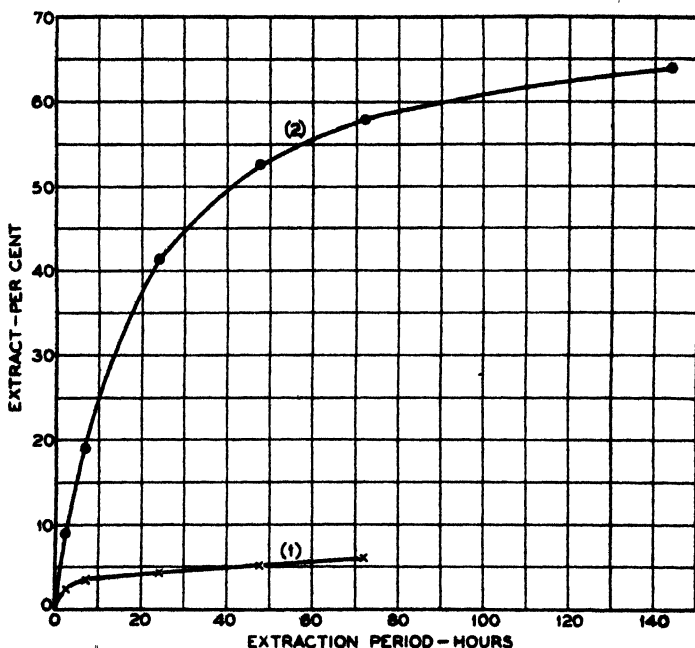


FIG. 7. Effect of alcohol on the solubility of gel rubber in hexane: (1) gel rubber in hexane; (2) gel rubber in hexane plus 10 per cent of absolute ethyl alcohol.

rubber molecules might also occur. There is, however, no concrete evidence available to indicate such a change.

SWELLING IN SOLVENTS

The literature contains many references to the swelling of crude rubber in various organic solvents. Values ranging from a few hundred to a few thousand per cent swelling are to be found. Our experience has been that the swelling in a given solvent is a property of the gel and is dependent upon the amount and nature of this gel present.

When the residual gel from the complete extraction of crepe by hexane was treated with a mixture of hexane containing 15 per cent of acetone, 22

per cent of this gel dissolved in 2 hr. The rubber was precipitated from solution with acetone, and the acetone was completely removed in a stream of nitrogen at room temperature. A 1.8-g. sample of this rubber was covered with 300 cc. of hexane. *No rubber* diffused into the hexane, but the rubber absorbed all of the solvent, and it had the properties of a thick stringy gel on shaking. Before solution the gel rubber had swelled about 2000 per cent in hexane; however, after the peptizing treatment and removal of the peptizing agent (i.e., acetone), the swelling reached a point of over 16,000 per cent. About all one can say definitely as regards this experiment is that some change has taken place in the gel upon conversion to sol and reconversion to gel. Addition of a little acetone or alcohol, with shaking, quickly changed the gel completely to sol, since the liquid became very mobile.

Sol rubber normally present in crude rubber is defined as that rubber which is soluble in light petroleum solvents. This rubber, as previously shown (1), originates through oxidation of the gel in latex assisted by mechanical breakdown on the washing rolls on the estate. It can be converted to a gel through some type of vulcanization. The sol rubber resulting from the peptizing of gel with a polar solvent is a different type of sol, which reverts to gel upon removal of the polar solvent and back again to sol upon addition of a polar solvent to the hexane. These observations lead to the possible conclusion that natural rubber gel is the result of strong association forces between the high-polymeric rubber molecules. This force may exist between active double bonds in certain positions, which upon oxidation cause the splitting of the macromolecule and a reduction of molecular weight to the sol range, i.e., less than about 200,000. After these active double bonds are satisfied by oxidation, gelation will not take place except upon vulcanization with sulfur or some other agent that serves to link the sol molecules to form a gel.

The possibility that the high strength and low solubility of gel are due mainly to its high molecular weight must also be given serious consideration. This would accord with the fact that all polymers show increased strength and decreased solubility upon increased polymerization.

CONCLUSIONS

n-Hexane is shown to be an excellent solvent for fractionating sol from crude rubber and for viscosity molecular weight determinations. The instability of high-molecular rubber in tetralin and the difficulty of dispersing gel in benzene are cited as objections to these solvents for determining the average molecular weight of crude rubber.

The molecular weight calculated by the Staudinger formula

$$M = \frac{\eta_{sp}}{C \cdot 3 \times 10^{-4}}$$

has been shown to vary with concentration to a much greater extent than the molecular weight based on the Arrhenius equation

$$M' = \frac{\log_{10} \eta_r \cdot 10^4}{C}$$

The average molecular weight of crude rubber determined by the viscosity method is of questionable value on account of the insoluble gel present. The molecular weight distribution of polyprenes in crude rubber depends on the proportion of sol and gel present, which has already been shown to vary widely.

The solubility and rate of diffusion of sol into hexane from crepe rubber decrease as its molecular weight increases. Sol rubber of a molecular weight of 210,000 is practically insoluble and diffuses very slowly into hexane. The average molecular weights of sol rubber fractions from unmilled crepe range from about 60,000 to 210,000. Gel rubber has a molecular weight greater than 210,000.

Milling results in the oxidative breakdown of rubber hydrocarbon macromolecules to a much smaller but more uniform size. Hot milling results in higher average molecular weights with a different distribution than that produced by cold milling.

A polar solvent such as absolute ethyl alcohol is shown to reduce immediately the viscosity of rubber solutions in hexane. The addition of alcohol or acetone to hexane is shown to peptize gel rubber. These phenomena are explained on the basis of a reduction of association or van der Waals forces between the long-chain molecules. This peptized gel can be converted to hexane-insoluble gel by removing the peptizing agent. Swelling of rubber in an organic solvent is shown to depend upon the nature of the gel present. A gel that has been peptized shows greatly increased swelling in hexane when the peptizing agent has been removed.

REFERENCES

- (1) KEMP, A. R., AND PETERS, H.: *J. Phys. Chem.* **43**, 923 (1939).
- (2) STAUDINGER, H.: *Die hochmolekularen organischen Verbindungen*. Julius Springer, Berlin (1932).
- (3) STAUDINGER, H., AND BONDY, H. F.: *Ann.* **488**, 153 (1931); *Rubber Chem. Tech.* **5**, 278 (1932).

CERTAIN PROPERTIES OF LONG-CHAIN COMPOUNDS AS FUNCTIONS OF CHAIN LENGTH^{1, 2}

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In this paper the dependence on chain length of the heat content, heat capacity, entropy, and free energy of typical long-chain compounds in the solid, liquid, and gaseous states will be considered theoretically and the relationships deduced will be applied to changes of state. Comparisons will be made with experimental data for normal paraffins. Extension to other cases can readily be made.

HEAT CONTENT AND HEAT CAPACITY

The heat content per mole of a long-chain compound is given by the following equations, for the solid, liquid, and gaseous states, respectively:

$$H_s = E_{\infty} + E_{\text{vib}} + E_{\text{rot}} - E_{\text{bond}} - E_{\text{vdW}} + PV \quad (1)$$

$$H_L = E_{\infty} + E'_{\text{vib}} + E'_{\text{rot}} - E'_{\text{bond}} - E'_{\text{vdW}} + PV' \quad (2)$$

$$H_g = E_{\infty} + E''_{\text{vib}} + E''_{\text{trans}} + E''_{\text{rot}} - E''_{\text{bond}} - E''_{\text{vdW}} + PV'' \quad (3)$$

E_{∞} is the energy that a mole of the substance would have at the absolute zero, if the molecules were completely dissociated into widely separated atoms.

E_{vib} , E'_{vib} , and E''_{vib} are the vibrational energies per mole. For the solid and liquid they should be nearly equal at the same temperature. In the gas the vibrational energy is all intramolecular. For the liquid or solid state there is also an energy of vibration of each molecule as a whole relative to its neighbors. This intermolecular vibrational energy should approximately equal the translational energy ($3/2 RT$) of the molecules in the gaseous state:

$$E_{\text{vib}} = E'_{\text{vib}} = E''_{\text{vib}} + E''_{\text{trans}} \quad (4)$$

E_{rot} , the rotational energy in the solid state, arises almost entirely from rotation of atoms or small groups of atoms, rather than from rotation of

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the molecule as a whole. Except for a small correction for the chain ends, therefore, E_{rot} should be proportional to the number of repeating units:

$$E_{\text{rot}} = a_0 + an \quad (5)$$

In the liquid there is a larger amount of rotation of this sort, and for short chains there is also some rotation of the whole molecule:

$$E'_{\text{rot}} = a'_0 + a'n \quad (6)$$

$$a' > a \quad (7)$$

(Strictly, a'_0 is not independent of n . It should decrease, however, as n increases, approaching a small, constant value.) For the gaseous state, similarly,

$$E''_{\text{rot}} = a''_0 + a''n \quad (8)$$

$$a'' \approx a' \quad (9)$$

$$a''_0 \approx \frac{3}{2} RT + a'_0 \quad (10)$$

E_{bond} , E'_{bond} , and E''_{bond} , the sums of the bond energies, may be considered equal for the three states:

$$E_{\text{bond}} = E'_{\text{bond}} = E''_{\text{bond}} \quad (11)$$

(For a long-chain molecule, obviously, this sum is proportional to the chain length.)

E_{vdw} , E'_{vdw} , and E''_{vdw} , the van der Waals energy terms, result from interactions (chiefly attractions) between atoms not directly bonded together. In the solid and liquid states these are both intermolecular and intramolecular; in a gas they are exclusively intramolecular, except insofar as there are deviations from the perfect gas laws. Crystalline normal paraffins (12) and some other long-chain compounds in the solid state (e.g., polymethylene oxide (8) and polyesters (5, 6)) contain parallel, extended, zigzag chains. Many others (e.g., many vinyl polymers) consist of chains which are kinked in a more or less random manner. Such kinked molecules are doubtless the rule in the liquid state. For both extended and kinked models, the van der Waals energy contribution of each unit in the chain would be expected to be independent of the chain length, except for a small end correction:

$$E_{\text{vdw}} = b_0 + bn \quad (12)$$

$$E'_{\text{vdw}} = b'_0 + b'n \quad (13)$$

In general,

$$b > b' \quad (14)$$

while b_0 and b'_0 are of the order of magnitude of b and b' but probably smaller. In the liquid there are, on the average, fewer interatomic "contacts" than in the solid. Also, the average interatomic distance is greater and so the average attraction energy per contact is smaller.

In the gaseous state the van der Waals attractions between atoms not directly bonded together tend to make a flexible long-chain molecule coil up into a ball (11, 1). An atom in the interior of such a ball molecule would have practically the same van der Waals energy as if the molecules were in the liquid state at the same temperature. An atom in the surface of the ball, on the other hand, is not completely surrounded by other atoms. Hence its van der Waals energy is less than it would be in the liquid.

A large sphere composed of n closely packed atoms (each with twelve close neighbors) would have a surface area of $2^{1/3}3^{2/3}\pi^{1/3}d_0^2n^{2/3}$, d_0 being the distance between the centers of adjacent atoms. For the lowest energy (greatest stability), each surface atom would have six other surface atoms and three interior atoms adjacent to it. It would occupy a surface area of $2^{-1/3}3^{1/2}d_0^2$. The number of surface atoms is then $2^{4/3}3^{1/6}\pi^{1/2}n^{2/3}$ or $4.43n^{2/3}$. Assuming approximate close-packing of atoms in both liquid and gaseous states, one deduces, therefore, as a limiting law for large n ,

$$E''_{vdw} = b''_0 + b''n - c''n^m \quad (15)$$

where

$$b'' \approx b' \quad (16)$$

$$c'' \approx \frac{4.43b'}{4} \approx 1.11b' \quad (17)$$

$$m = \frac{2}{3} \quad (18)$$

Also, b'_0 and b''_0 are probably not very different.

The last terms in equations 1 and 2 may ordinarily be neglected, since the molal volumes, V and V' , are relatively small and nearly equal:

$$PV \approx PV' \approx 0 \quad (19)$$

The PV'' term in equation 3 is important at high temperatures or pressures, P . As a first approximation,

$$PV'' \approx RT \quad (20)$$

Substitution into equations 1, 2, and 3 and subtraction gives the variation with n to be expected for the heats of fusion and vaporization, on the assumption that all are measured at the same temperature:

$$(\Delta H_f)_T = H_L - H_S = (a'_0 - a_0 + b_0 - b'_0) + (a' - a + b - b')n \quad (21)$$

$$(\Delta H_v)_T = H_G - H_L = (\frac{1}{2}RT + b'_0 - b''_0) + 1.11b'n^{2/3} \quad (22)$$

Experimentally, heats of fusion of different compounds are not measured at the same temperature, but at the melting points, hence equation 21 is directly applicable only when n is so large that all the compounds being compared have nearly the same melting point, $T_{f, \max}$. To make the relation between the heats of fusion at the melting points applicable to all values of n , one must make a correction for the difference in heat capacities:

$$(\Delta H_f)_{T_f} = (\Delta H_f)_{T_{f, \max}} - \int_{T_f}^{T_{f, \max}} [C_p(l) - C_p(s)] dT \quad (23)$$

Equation 22 is compared with the experimental heats of vaporization of paraffins at 298°K. in figure 1. The values plotted are those chosen

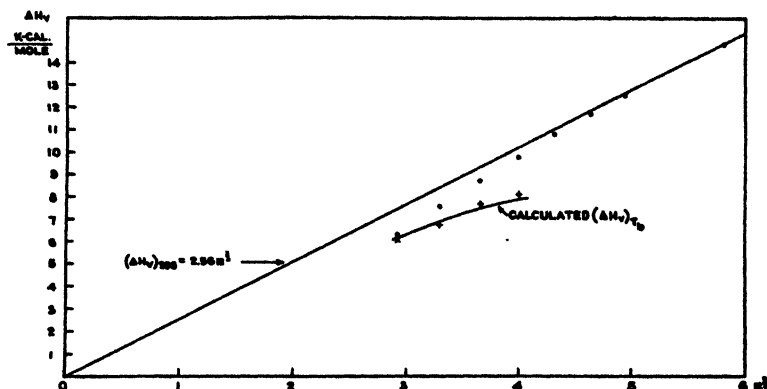


FIG. 1. Heats of vaporization of normal paraffin hydrocarbons at 298°K. and at the boiling point. O, Rossini, at 298°K.; X, Sage, Lacey, and Schaafsma, at T_b ; +, Schultz, at T_b . The straight line represents the equation $(\Delta H_v)_{298} = 2.56n^{2/3}$. The other curve represents $(\Delta H_v)_{T_b}$, calculated on the assumption that Rossini's $(\Delta H_v)_{298}$ values are correct.

as "best" by Rossini (17) after a critical survey of the literature. The experimental curve approaches proportionality with $n^{2/3}$ as n increases.

To compare heats of vaporization at the normal boiling points, it is again necessary to correct for the heat capacity differences:

$$(\Delta H_v)_{T_b} = (\Delta H_v)_{298} + \int_{298}^{T_b} [C_p(g) - C_p(l)] dT \quad (24)$$

Since

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (25)$$

the relationships given above for the terms in the expressions for the heat content lead to the conclusions that the heat capacities in the solid, liquid,

and gaseous states, respectively, should depend on the chain length in the following manner:

$$C_p(s) = f_0 + fn \quad (26)$$

$$C_p(l) = f'_0 + f'n \quad (27)$$

$$C_p(g) = f''_0 + f''n + g''n^{2/3} \quad (28)$$

Here f_0 , f , g'' , etc. are functions of temperature but not of n . The last term in equation 28 would be expected to be small, the change in van der Waals energy with temperature being small relative to the change with

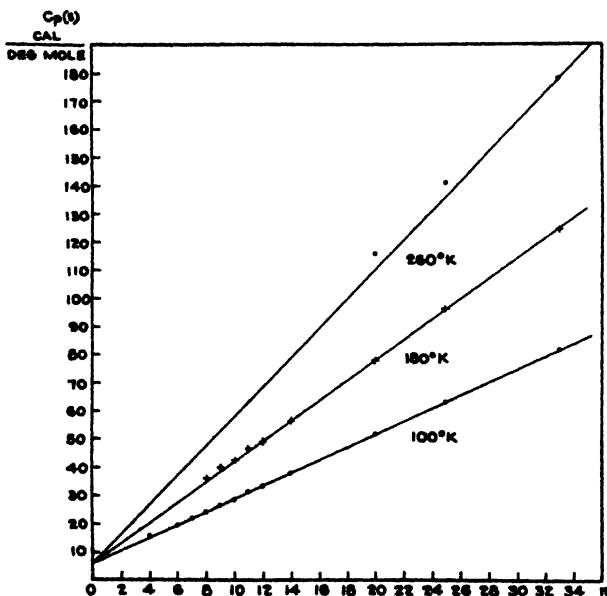


FIG. 2. Heat capacities of crystalline normal paraffin hydrocarbons. Variation of $C_p(s)$ with n at various temperatures. Data are those of Parks and coworkers.

temperature of the oscillational and rotational energy. Hence, approximately,

$$C_p(g) = f''_0 + f''n \quad (29)$$

Experimental data for solid and liquid normal paraffins (9, 13, 14, 15, 18) agree well with equations 26 and 27, as shown in figures 2 and 3. Over the temperature ranges studied, one can put

$$f_0 = 8 \text{ cal.} \quad (30)$$

(regardless of the crystal form), and

$$f'_0 = 0 \quad (31)$$

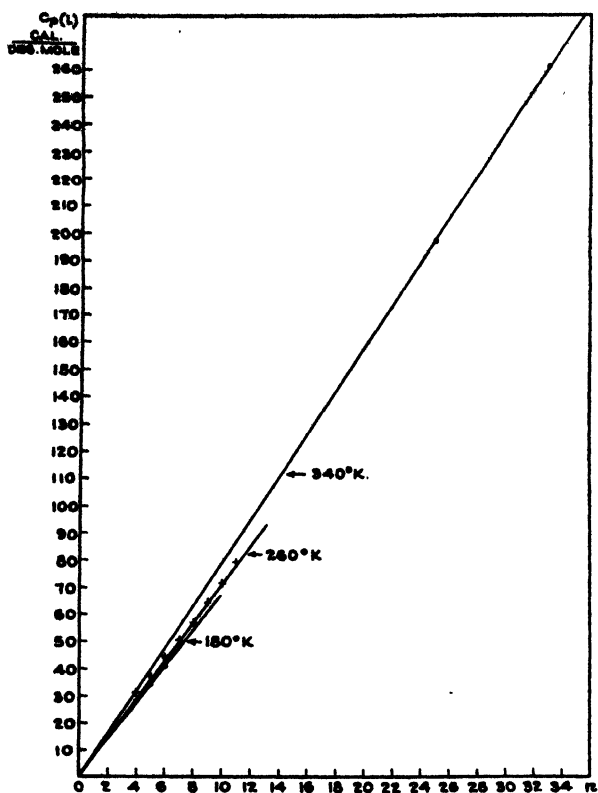


FIG. 3. Heat capacities of liquid normal paraffin hydrocarbons. Variation of $C_p(l)$ with n at various temperatures. Data are those of Parks and coworkers.

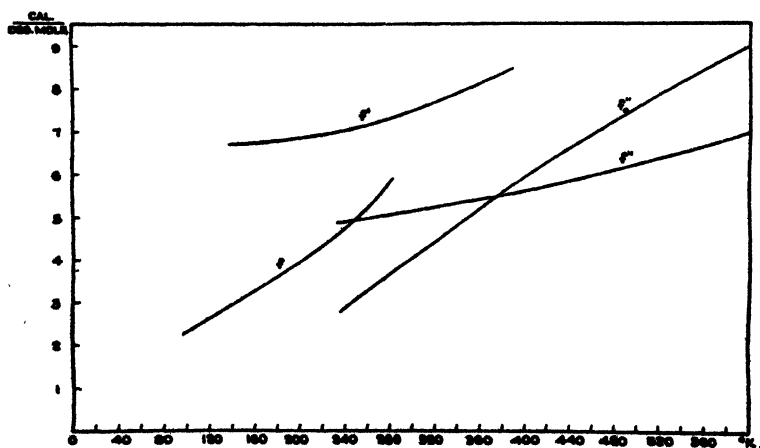


FIG. 4. Variation of the heat capacity functions for normal paraffin hydrocarbons with the temperature. $C_p(s) = 6 + fn$; $C_p(l) = f'n$; $C_p(g) = f''_0 + f''n + \frac{h^2 P}{T^3} n^2$.

while f and f' depend on temperature in the manner indicated in figure 4. It may be noted that the function for the liquid agrees well with the relation

$$f' = 6.57 + 0.033 \cdot 10^{-6} T^3 \quad (32)$$

between 140°K. and 380°K.

As Edmister (3) has pointed out, the data available for the heat capacity of paraffins (having $n \geq 3$) in the gaseous state between 250°K. and 600°K. are in fair agreement with the relation

$$C_p = (2.56 + 0.51n) + (0.0042 + 0.0130n)T \quad (33)$$

This can obviously be rearranged to

$$C_p = (2.56 + 0.0042T) + (0.51 + 0.0130T)n \quad (34)$$

in agreement with equation 29.

Equations for the temperature dependence which are probably more accurate have been obtained by Bennewitz and Rossner (2), using Einstein functions. Reexpressing their results in terms of power series in T , Fugassi and Rudy have arrived at equations, which, for normal paraffins, reduce to

$$C_p = f_0'' + f''n + \frac{h''P}{T^3} n^2 \quad (35)$$

where

$$f_0'' = 4.43 + 0.324 \cdot 10^{-3} T + 6.543 \cdot 10^{-6} T^2$$

and

$$f'' = -2.784 + 25.98 \cdot 10^{-3} T - 10.647 \cdot 10^{-6} T^2$$

The n^2 term is a correction, usually negligible, for deviations from the perfect gas law. The quantity h'' is a function of n which seems to be approaching a constant value of about $0.5 \cdot 10^6$ as n increases (figure 5).

The difference between equations 34 and 35 is illustrated, for two values of n , in figure 6.

Calculations show that the heat capacity correction term in equation 23 for the heats of fusion is always relatively small and decreases as the length of the chain increases. The simple equation

$$\Delta H_f = A + Bn \quad (36)$$

should, therefore, be applicable to heats of fusion measured at the melting points, except when n is quite small. The experimental results are in agreement with this conclusion (figure 7).

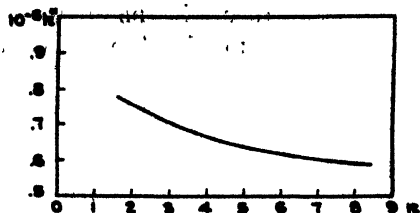


FIG. 5. Variation with n of the function h'' in the gas imperfection correction term ($h''Pn^3/T^3$) for the heat capacities of gases.

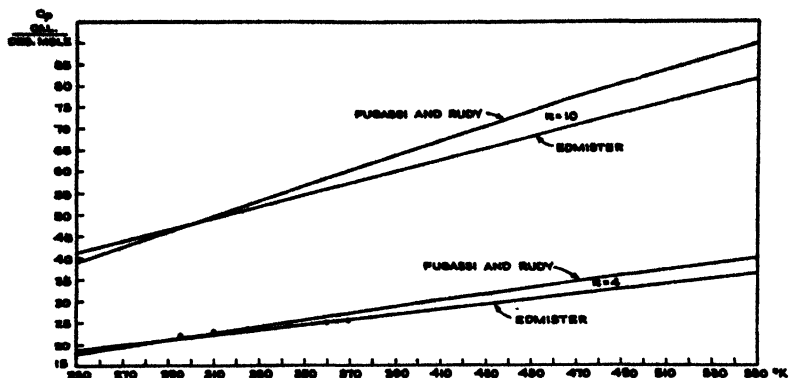


FIG. 6. Comparison of Edmister's equation with that of Fugassi and Rudy for the heat capacities of normal paraffins. Heat capacities of gaseous normal butane and normal decane. Experimental points are from Sage and Lacey.

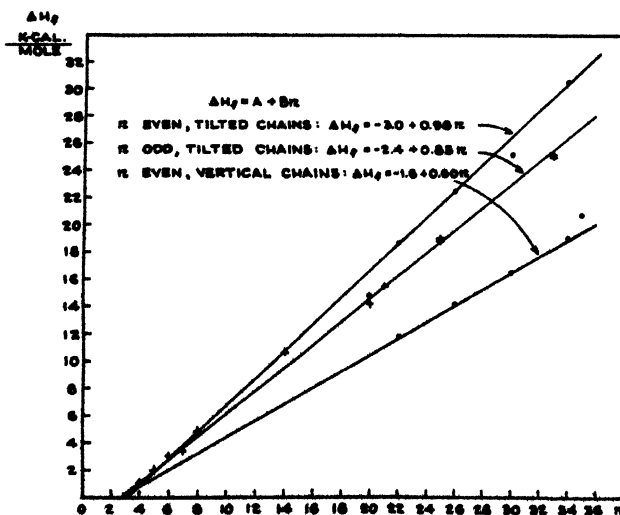


FIG. 7. Heats of fusion of normal paraffins. +, Parks and coworkers; O, Garner, Van Bibber, and King.

The heat capacity correction in equation 24 for the heats of vaporization, on the other hand, is not negligible. Assuming Rossini's values for ΔH_v at 298°K. to be correct and making use of equations 27, 31, 32, and 35 and also figure 5, the lower curve in figure 1, representing ΔH_v at the boiling point, has been obtained. The agreement with the experimental points (19, 20) is not bad.

ENTROPY

Entropy is a measure of randomness. For convenience, the entropy per mole of a long-chain compound in the solid or liquid state may be divided into four parts, according to the source of the randomness: (1) randomness resulting from the temperature vibrations of each molecule as a whole; (2) randomness of position and orientation of each molecule as a whole; (3) randomness resulting from alternative orientations of the chain bonds relative to each other and from more or less free rotation about the bonds; and (4) randomness due to vibrations of the atoms in each molecule relative to their neighbors.

$$S = S_{ev} + S_{p\&o} + S_{ir} + S_{iv} \quad (37)$$

$$S' = S'_{ev} + S'_{p\&o} + S'_{ir} + S'_{iv} \quad (38)$$

For the gaseous state, similarly,

$$S'' = S''_{ir} + S''_{or} + S''_{ir} + S''_{iv} \quad (39)$$

the first two terms measuring the randomness resulting from the translational and the rotational motion, respectively, of the molecule as a whole.

The entropy of external vibrations, S_{ev} and S'_{ev} , is a function of the temperature, but (for non-rigid molecules) may be assumed to be approximately independent of chain length at any given (not too low) temperature, both in the solid and in the liquid:

$$S_{ev} = \alpha_0 \quad (40)$$

$$S'_{ev} = \alpha'_0 \quad (41)$$

As the immediate environment of each atom or group is about the same in the liquid as in the solid,

$$\alpha_0 \approx \alpha'_0 \quad (42)$$

(Since, for long-chain molecules, this term is relatively small, considerable inaccuracy in this assumption does not matter.)

The entropy of position and orientation, $S_{p\&o}$ and $S'_{p\&o}$, is also temperature-dependent, but for long molecules practically independent of chain length:

$$S_{p\&o} = \beta_0 \quad (43)$$

$$S'_{p\&o} = \beta'_0 \quad (44)$$

If the solid is crystalline, β equals zero; otherwise, it is finite. The value for the liquid, as a rule and perhaps always, is greater than that for the solid:

$$\beta'_0 > \beta_0 \quad (45)$$

For large values of n , both the first and the second entropy terms in equations 37 and 38 can be neglected.

The entropy of internal randomness, S_{ir} , S'_{ir} , and S''_{ir} , is a function of both temperature and chain length. At a given temperature it should be proportional to n (except for a small end correction), the addition of one unit to the chain increasing the entropy the same amount, regardless of the length of the chain:

$$S_{ir} = \gamma_0 + \gamma n \quad (46)$$

$$S'_{ir} = \gamma'_0 + \gamma' n \quad (47)$$

$$S''_{ir} = \gamma''_0 + \gamma'' n \quad (48)$$

Each C—C bond in a paraffin chain has three alternative equilibrium orientations relative to the preceding bonds in the chain. If these were equally probable, the entropy of internal randomness of a mole of rigid paraffin molecules would be $R(\ln 3)(n - 3)$ or, with n large, $R(\ln 3)n$. Actually, especially in the solid and liquid states, the three orientations are not equally probable. On the other hand, since the potential energy minima are not sharp, oscillations about the equilibrium orientations and (especially at high temperatures) rotations over the energy humps between them occur. This increases the entropy of internal randomness, but leaves it still proportional to n . Semi-quantitative calculations (10) have led to the value 8.9 for the proportionality constant, for a normal paraffin chain at 25°C., on the assumption of free rotation and have shown that restricting potentials of 3000 cal. per mole or less would not alter this constant by much. It is probably correct to write

$$\gamma < \gamma' < \gamma'' < 8.9 \quad (49)$$

The entropy of internal vibrations, S_{iv} and S'_{iv} , should also be proportional to n , for long chains:

$$S_{iv} = \delta_0 + \delta n \quad (50)$$

$$S'_{iv} = \delta'_0 + \delta' n \quad (51)$$

$$S''_{iv} = \delta''_0 + \delta'' n \quad (52)$$

For normal paraffins at 25°C., using the frequency assignments of Pitzer (16), the proportionality constant has been calculated (10) to be about

1.8. This factor should be only slightly dependent on the state, except in cases where intermolecular attractions are strong. Hence,

$$\delta \approx \delta' \approx \delta'' \approx 1.8 \quad (53)$$

The translational entropy, S_{tr}'' , has been shown (10), using well-known, generally accepted equations, to be given, at a definite temperature and pressure, by an equation of the form

$$S_{tr}'' = \epsilon_0'' + \epsilon'' \ln n \quad (54)$$

where

$$\epsilon'' = \frac{3R}{2} \approx 3.0 \quad (55)$$

and, for normal paraffins at 298°K. and 1 atmosphere,

$$\epsilon_0'' = 33.8 \quad (56)$$

The entropy, S_{or}'' , due to rotation of the molecule as a whole, obeys (10) an equation of similar form:

$$S_{or}'' = \zeta_0'' + \zeta'' \ln n \quad (57)$$

Hypothetically, assuming the molecular chains to be so coiled as to give each molecule a spherical shape, with an internal density equal to that in the liquid, one can calculate, again for a paraffin at 298°K.,

$$\zeta_0'' = 20.7 \quad (58)$$

and

$$\zeta'' = \frac{5R}{2} \approx 5.0 \quad (59)$$

If one assumes, instead, complete randomness of kinking (giving non-spherical, less dense molecules), constants which are slightly different, but not markedly so, are computed (10).

Substituting into equations 37, 38, and 39, one now obtains

$$S = (\alpha_0 + \beta_0 + \gamma_0 + \delta_0) + (\gamma + \delta)n \quad (60)$$

$$S' = (\alpha'_0 + \beta'_0 + \gamma'_0 + \delta'_0) + (\gamma' + \delta')n \quad (61)$$

$$S'' = (\gamma_0'' + \delta_0'' + \epsilon_0'' + \zeta_0'') + (\gamma'' + \delta'')n + (\epsilon'' + \zeta'') \ln n \quad (62)$$

As shown in figures 8 and 9, the entropies calculated from the experimental data on liquid and gaseous paraffins are in agreement with equations of the form of equations 61 and 62.

From equations 60 and 61 it follows that the entropy of fusion *at the same temperature for all values of n* should be a linear function of n . Since

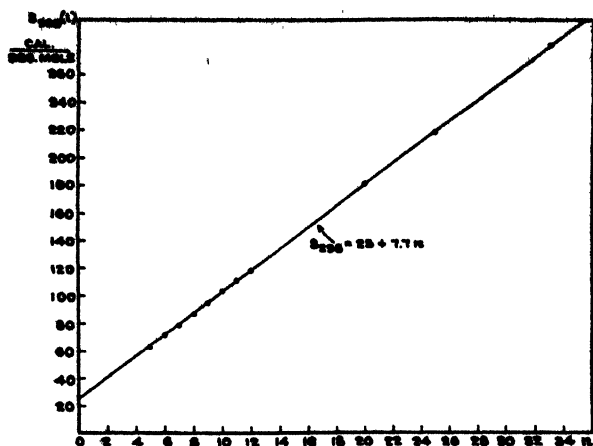


Fig. 8. Entropies of liquid normal paraffins (data from Parks and coworkers)

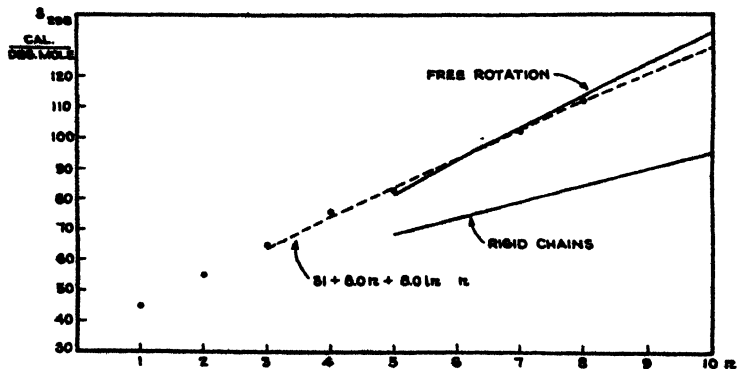


Fig. 9. Entropies of gaseous normal paraffin hydrocarbons

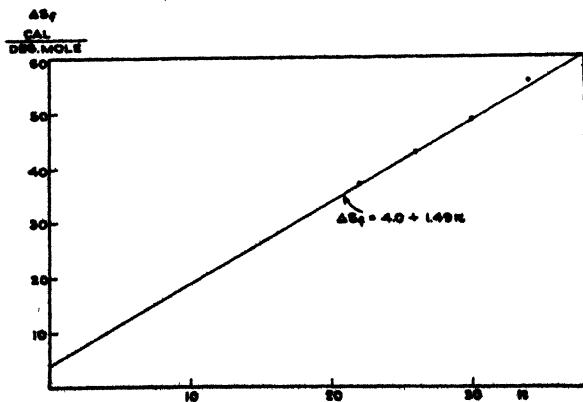


Fig. 10. Entropies of fusion of normal paraffin hydrocarbons. α -form. Data are those of Garner, Van Bibber, and King.

the correction for temperature differences⁷ is not large and since it is reasonable to suppose that the change in entropy of fusion with temperature is linear with respect to n , one should expect the entropy of fusion at the melting point to obey a similar law:

$$\Delta S_f = C + Dn \quad (63)$$

This is in line with the experimental results of Garner, Van Bibber, and King (7) (figure 10).

For the entropy of vaporization at a uniform temperature, a relation of the form

$$\Delta S_v = K + Ln + M \ln n \quad (64)$$

is similarly deduced. At the boiling point, according to Trouton's rule, the entropy of vaporization varies but little with n .

FREE ENERGY, MELTING POINT, BOILING POINT, VAPOR PRESSURE

From the relation

$$\Delta F = \Delta H - T\Delta S \quad (65)$$

and equations 21, 22, 63, and 64, one obtains for the differences in free energy between solid and liquid and between liquid and gas, at any given temperature,

$$F_L - F_s = P + Qn \quad (66)$$

and

$$F_g - F_L = U + Vn^{2/3} - Wn - X \ln n \quad (67)$$

P , Q , U , V , W , and X are functions of T but not of n .

At the melting point, the free energy change on fusion is zero. From equations 65, 36, and 63,

$$T_f = \frac{\Delta H_f}{\Delta S_f} = \frac{A + Bn}{C + Dn} \quad (68)$$

Garner and coworkers (7) have shown that an equation of this form fits the experimental data very well for hydrocarbons (also acids and esters). For large n , $1/T_f$, minus a constant, is proportional to $1/n$ (figure 11).

If the heats of vaporization at the boiling points were proportional to $n^{2/3}$, like those at a uniform temperature (equation 22), then Trouton's rule of constant entropy of vaporization at the boiling point would imply that the boiling point also is proportional to $n^{2/3}$. Since the heat of vaporization at T_b increases less rapidly than $n^{2/3}$, however (figure 1), so also does the boiling point (figure 12). By means of the specific heat

curves for the liquid and gas or the equations therefor, boiling point values in good agreement with experiment can readily be calculated, but only

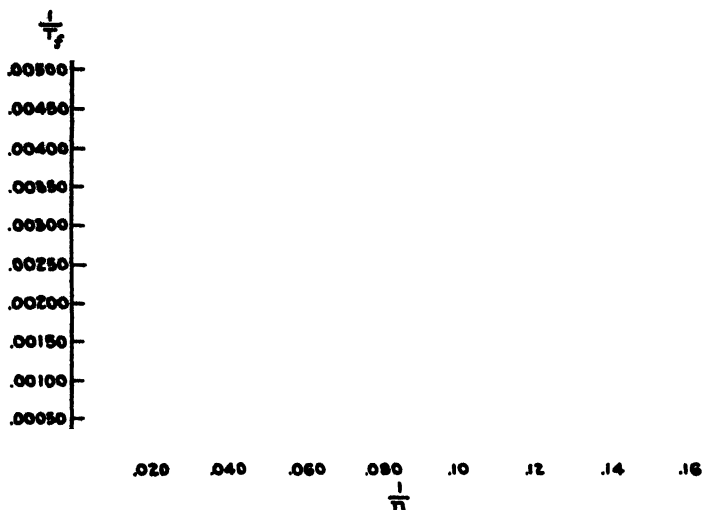


FIG. 11. Melting point data for normal paraffins

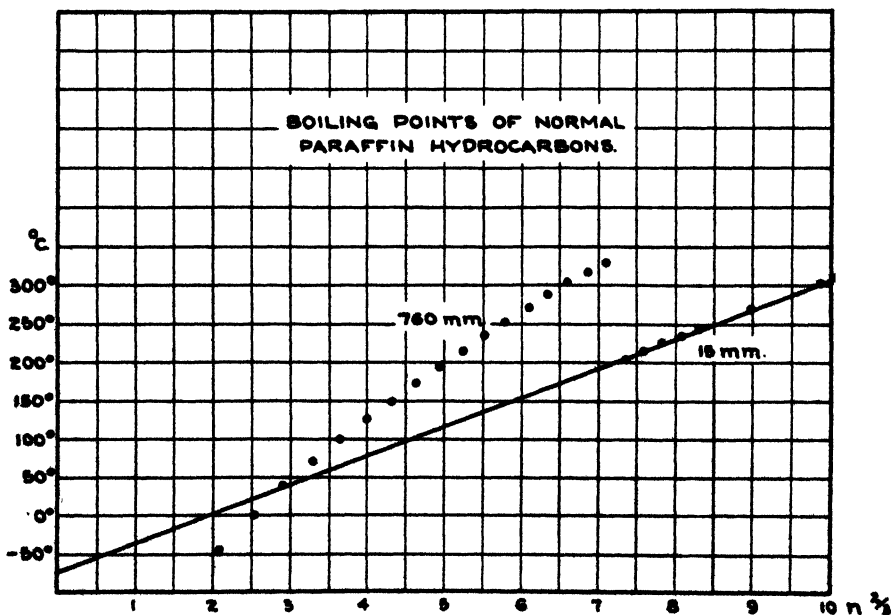


FIG. 12. Boiling points of normal paraffin hydrocarbons

over a limited range, because of the limited amount of data now available on the specific heats of the liquids.

To compare vapor pressures of a series of long-chain compounds at a uniform temperature, one may use the relation

$$\Delta F_v = \Delta H_v - T\Delta S_v = -RT \ln p \quad (69)$$

Substituting equation 67, one obtains

$$\ln p = -\frac{U}{RT} - \frac{V}{RT} n^{2/3} + \frac{W}{RT} n + \frac{X}{RT} \ln n \quad (70)$$

The experimental data for the paraffins (from *International Critical Tables* and *Landolt-Börnstein Tabellen*) approach agreement, as n increases, with an equation of this form, in which the constants are derived from those in the equations in figures 1, 8, and 9 (see figure 13). The deviations for small n are due almost entirely to the deviations of ΔH_v from proportionality with $n^{2/3}$ (figure 1).

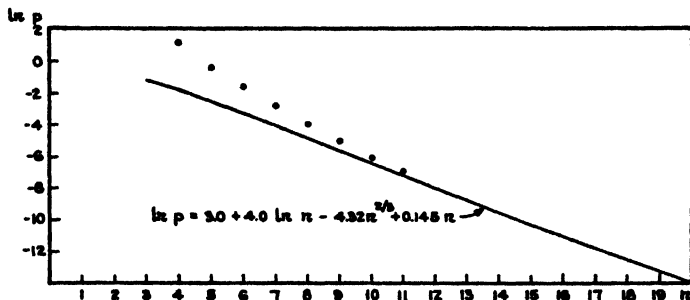


FIG. 13. Vapor pressures of liquid normal paraffin hydrocarbons at 298°K.

SUMMARY

From considerations which are largely qualitative in nature certain conclusions have been reached regarding the variation with chain length of various properties,—heat content, entropy, heat of fusion, heat of vaporization, vapor pressure,—of long-chain compounds at constant temperature. With the aid of experimental heat capacity data, expressions have been derived for the dependence on chain length of the melting point, heat of fusion and entropy of fusion at the melting point, and heat of vaporization at the boiling point. The variation of boiling point with chain length has also been briefly discussed.

The conclusions reached have been tested, where possible, with experimental data for normal paraffin hydrocarbons.

The writer is glad to express his thanks to Dr. F. D. Rossini of the National Bureau of Standards for permission to use his unpublished heat of vaporization values, and also to Miss Dorothy Owen for much help with the calculations leading to the results reported here.

REFERENCES

- (1) ATEN, A. H. W.: J. Chem. Phys. **5**, 264 (1937).
- (2) BENNEWITZ, K., AND ROSSNER, W.: Z. physik. Chem. **B99**, 126 (1938).
- (3) EDMISTER, W. C.: Ind. Eng. Chem. **30**, 352 (1938).
- (4) FUGASSI, P., AND RUDY, C. E., JR.: Ind. Eng. Chem. **30**, 1029 (1938).
- (5) FULLER, C. S., AND ERICKSON, C. L.: J. Am. Chem. Soc. **59**, 344 (1937).
- (6) FULLER, C. S., AND FROSCH, C. J.: J. Phys. Chem. **43**, 323 (1939).
- (7) GARNER, W. E., VAN BIBBER, K., AND KING, A. M.: J. Chem. Soc. **1931**, 1533.
- (8) HENGSTENBERG, J.: Ann. Physik **84**, 245 (1927).
- (9) HUFFMAN, H. M., PARKS, G. S., AND BARMORE, M.: J. Am. Chem. Soc. **53**, 3876 (1931).
- (10) HUGGINS, M. L.: Unpublished calculations, reported at the Ninety-sixth Meeting of the American Chemical Society, held in Milwaukee, Wisconsin, September, 1938.
- (11) LANGMUIR, I.: In *Colloid Chemistry*, edited by Jerome Alexander, Vol. I, p 525. The Chemical Catalog Co., Inc., New York (1926).
- (12) MÜLLER, A.: Proc. Roy. Soc. (London) **A120**, 437 (1938).
- (13) PARKS, G. S., AND HUFFMAN, H. M.: J. Am. Chem. Soc. **52**, 4381 (1930).
- (14) PARKS, G. S., HUFFMAN, H. M., AND THOMAS, S. B.: J. Am. Chem. Soc. **52**, 1032 (1930).
- (15) PARKS, G. S., AND LIGHT, D. W.: J. Am. Chem. Soc. **56**, 1511 (1934).
- (16) PITZER, K. S.: J. Chem. Phys. **5**, 473 (1937).
- (17) ROSSINI, F. D.: Private communication.
- (18) SAGE, B. H., AND LACEY, W. N.: Ind. Eng. Chem. **27**, 1484 (1935).
- (19) SAGE, B. H., LACEY, W. N., AND SCHAAFSMA, J. G.: Ind. Eng. Chem. **27**, 48 (1935).
- (20) SCHULTZ, J. W.: Ind. Eng. Chem. **21**, 557 (1929).
- (21) SPAGHT, M. E., THOMAS, S. B., AND PARKS, G. S.: J. Phys. Chem. **36**, 882 (1932).

COMPUTATION OF MATHEMATICAL TABLES

The following statement¹ with reference to a project for the computation of mathematical tables under the Work Projects Administration may be of interest to the readers of *The Journal of Physical Chemistry*:

A Project for the Computation of Mathematical Tables, sponsored by Dr. Lyman J. Briggs, Director of the National Bureau of Standards, is being conducted by the Work Projects Administration for the City of New York. The Project has been in operation since January 1, 1938, under the technical supervision of Dr. Arnold N. Lowan.

An agenda of the Project, listing the tables completed, in progress, and under consideration, is given below:

Completed tables

1. A table of exponentials for the following ranges, intervals, and number of decimals:

<i>Range</i>	<i>Interval</i>	<i>Number of decimals</i>
-2.5000 to 1.0000	0.0001	18
1.0000 to 2.5000	0.0001	15
2.500 to 5.000	0.001	15
5.00 to 10.00	0.01	12

2. A table of sines and cosines for the range from 0 to 25 radians at intervals of 10^{-3} to eight places of decimals.

3. A table of the first ten powers of the integers from 1 to 1000.

Tables in progress

- A. Computations completed; manuscripts in process of preparation

1. A table of the functions—

$$Si(x) = \int_0^x \frac{\sin t}{t} dt; \quad Ci(x) = \int_{\infty}^x \frac{\cos t}{t} dt$$

$$Ei(x) = \int_{-\infty}^x \frac{e^t}{t} dt; \quad -Ei(-x) = \int_x^{\infty} \frac{e^{-t}}{t} dt$$

for the range between 0 and 2 at intervals of 10^{-4} to nine places of decimals.

2. A table of the functions defined in paragraph 1 for the range between 0 and 10 at intervals of 10^{-3} to nine significant figures.

3. A table of circular and hyperbolic sines and cosines for the range between 0 and 2 at intervals of 10^{-4} .

4. A table of natural logarithms of integers from 0 to 100,000 to sixteen places of decimals.

5. A table of natural logarithms of decimal numbers from 0.0000 to 10.0000 at intervals of 10^{-4} to sixteen places of decimals.

¹ Issued July 1, 1939.

6. A series of physical tables:

(a) $G = 1/\sqrt{1-\beta^2}$, for β ranging from 0 to 0.9997 at various intervals. This table also includes certain functions depending on G .

(b) Table of

$$N_\lambda = 2\pi c \lambda^{-4} \left(e^{\frac{c_2}{\lambda T}} - 1 \right)^{-1}$$

for λ ranging between 0.25 and 10 microns at various intervals, and for $T = 1000, 1500, 2000, 2500, 3000, 3500, 6000^\circ\text{K}$.

(c) Table of

$$J_\lambda = c_1 \lambda^{-5} \left(e^{\frac{c_2}{\lambda T}} - 1 \right)^{-1}$$

for $T = 1000^\circ\text{K}$., ranging from 0.5 to 20 microns at various intervals.

(d) Table of

$$N_{0-\lambda} = \int_0^\lambda N_\nu d\nu$$

and

$$J_{0-\lambda} = \int_0^\lambda J_\nu d\nu$$

for $T = 1000^\circ\text{K}$. Range of λ the same as for J_λ .

(e) Table of the ratios

$$\frac{J_{0-\lambda}}{J_{0-\infty}}, \quad \frac{N_{0-\lambda}}{N_{0-\infty}}, \quad \frac{J_\lambda}{(J_\lambda)_{\max}}, \quad \text{and} \quad \frac{N_\lambda}{(N_\lambda)_{\max}}$$

Range for λ same as under paragraph c.

B. Computations in progress

7. Table of the probability functions

$$\frac{2}{\sqrt{\pi}} e^{-x^2} \quad \text{and} \quad \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

for x ranging from 0 to 1 at intervals of 10^{-4} and from 1 to 6 at intervals of 10^{-1} .

8. Table of the probability functions

$$\sqrt{\frac{2}{\pi}} e^{-\frac{x^2}{2}} \quad \text{and} \quad \sqrt{\frac{2}{\pi}} \int_0^x e^{-\frac{t^2}{2}} dt$$

for x ranging between 0 and 1 at intervals of 10^{-4} and from 1 to 8.4 at intervals of 10^{-1} .

9. Table of Bessel functions $J_0(z)$ and $J_1(z)$ for complex arguments, $z = re^{i\theta}$, where r ranges from 0 to 10 at intervals of 0.01 and θ ranges from 0 to 90° at intervals of 5° .

10. Table of $\tan x$ and $\cot x$ for x ranging between 0 and 2 at intervals of 10^{-4} .

11. Table of the integrals

$$\int_0^1 x^k \sin n\pi x dx \quad \text{and} \quad \int_0^1 x^k \cos n\pi x dx$$

for $n = 0, 1, 2, 3, \dots, 100$ and $k = 0, 1, 2, 3, 4, 5$.

Tables under consideration

1. A 12-decimal place table of inverse tangents to radian measure. The table will include the following ranges: from 0 to 3 at intervals of 10^{-2} ; from 3 to 10 at intervals of 10^{-2} ; from 10 to 40 at intervals of 10^{-1} ; from 40 to 100 at intervals of 1; and from 100 to 1000 at intervals of 10.

2. Table of Bessel functions $J_{\pm 1/2}(z)$, $J_{\pm 3/2}(z)$, $J_{\pm 5/2}(z)$, $Y_0(z)$, $Y_1(z)$, and $K_{\pm 1/2}(z)$, for ranges and intervals similar to those for $J_0(z)$ and $J_1(z)$.

3. Table of

$$Q_n(x) = \sqrt{\frac{\pi}{2x}} \cdot J_{n+1/2}(x)$$

for x ranging between 0 and 10 at intervals of 0.01 and for $n = 1, 2, 3, \dots, 10$.

4. Table of gamma functions for complex arguments $a + bi$, where a and b range from 0 to 5 at intervals of 0.05.

5. Table of elliptic functions for arguments $z = x + iy$, where x and y range from 0 to $\pi/2$ at intervals of 0.01.

6. Table of the function

$$A(x, y) = \frac{1 - x^y}{1 - x}$$

where x ranges from 0 to 1 at intervals of 0.01 and y ranges from 0 to 4 at intervals of 0.01.

7. Table of temperature and density of stars, for "point-source" models.

The directors of the Project are anxious to hear from scientific colleagues concerning work in progress elsewhere, as well as concerning suggestions for new tables. All suggestions will receive careful consideration.

Communications concerning new tables or work in progress elsewhere should be addressed to Dr. Arnold N. Lowan, Chief Project Supervisor, Project for the Computation of Mathematical Tables, 475 Tenth Avenue, New York City, New York.

ERRATA

Volume 42, Number 4, April, 1938

Page 467: Five of the references should be corrected to read as follows:

- (3) BJERRUM: Z. anorg. allgem. Chem. 109, 275 (1920).
- (8) FRAZER AND MYRICK: J. Am. Chem. Soc. 36, 1907 (1916).
- (9) GUGGENHEIM: Phil. Mag. [7] 2, 538 (1926).
- (11) HARNED: J. Am. Chem. Soc. 40, 1461 (1918); 42, 1808 (1920).
- (17) SCATCHARD: J. Am. Chem. Soc. 43, 2387, 2406 (1921).

Volume 43, Number 6, June, 1939

Page 797: In equations 1 and 3 substitute " $\underline{\nu}\lambda m$ " for " $\nu\lambda m$ ".

Page 798: In the main heading and in the right-hand box heading of table 2 substitute " $\underline{\nu}$ " for " ν ".

Page 800: In the first and fourth lines under table 3 substitute " $\underline{\nu}$ " for " ν ".

NEW BOOKS

The War Gases. By MARIO SARTORI. Preface by G. BARGELLINI. Translated from the second enlarged Italian edition by L. W. MORRISON. 6 x 9 in.; xii + 360 pp.; 20 figures; 15 tables. New York: D. Van Nostrand Company, Inc., 1939. Price: \$7.50.

This book is a welcome addition to the library of chemical warfare. It is particularly valuable to students of chemical warfare who have been curious about the chemical, physical, physiopathological, and tactical reasons for the rather small number of chemical agents considered satisfactory for war use by the military services.

Doctor Sartori has been careful to present rather completely and clearly the properties that an effective war gas must have. He has not concerned himself with the non-toxic smokes, such as white phosphorus and titanium tetrachloride. He discusses the physiopathological properties and gives data on the relative effectiveness of many of the war gases. The physical and chemical properties are considered with respect to the tactical uses to which the gases might be put and to the ease of manufacture and handling under war conditions. The relationship between chemical structure and aggressive action, including the influence of the halogens, sulfur, arsenic, nitro groups, CN groups, and molecular structure on the war gas properties of chemical compounds are reviewed. He has included several methods of classification,—chemical and tactical,—which have been presented by various workers.

The book is most valuable for its complete data on more than sixty elements and compounds possessing properties making them possible war gases. Information is presented for each compound or element on its constitution, on laboratory methods of preparation, on the industrial method of manufacture where the compound has been produced industrially, and on its several properties.

M. C. ROGERS.

Ions, Electrons and Ionizing Radiations. By J. A. CROWTHER. Seventh edition. 6 x 9 in.; xi + 348 pp.; 117 figures; 17 tables. New York: Longmans, Green and Company, 1939. Price: \$4.00.

The earlier editions of this work are well known to students of electronics and nuclear physics or chemistry. It is intended as an elementary supplemental text for students who have had an introductory course in physics. The rapid increase in knowledge of the nucleus has necessitated extension of the text to include new sections on neutrons, positrons, and cosmic radiation.

S. C. LIND.

Experimental Methods in Gas Reactions. By A. FARKAS AND H. W. MELVILLE. 6 x 8½ in.; xv + 389 pp.; 266 figures. New York: The Macmillan Company, 1939.

All who have worked in the field of gas kinetics are familiar with the variety and the difficulty of the techniques that must be employed in preparing and handling gases under all the necessary conditions. The authors have performed a real service in collecting these, classifying them, and bringing them together for the first time under one cover.

The treatment is extensive, including kinetic gas theory, collisions, energy dis-

tribution, and elements of chemical kinetics. There is a chapter of one hundred pages on the technique of handling gases, such as the use of vacuum pumps, gauges, vacuum points, control and measurement of pressure and of temperature; the preparation and analysis of gases, including some isotopes; photochemical technique including sources, control, and measurement of radiation; methods and devices for measuring rates of reactions and factors of influence such as catalysis, illumination, and electric activation; and finally a section on explosive reactions.

Naturally a manual on such a comprehensive field can not pretend to be exhaustive, but the authors have exercised excellent judgment in their selections and have produced a manual that should be as useful to experimental kineticists as the well-known Ostwald-Luther manual was earlier to all physical chemists.

S. C. LIND.

Discovery of the Elements. By MARY ELVIRA WEEKS. Fourth edition. Easton, Pennsylvania: The Journal of Chemical Education, 1939. Price: \$3.00.

The fourth and enlarged edition of this splendid account of the discovery of the elements will be welcomed by every lover of the history of chemistry. The reviewer can second the statement of the *Scientific American*: "A rich mine of elementary chemical lore informatively but most readably written," if "and" be substituted for the word "but". There is no necessary antithesis between informative and readable, as Miss Weeks has convincingly proved.

In dealing with the elements the author has wisely not confined herself to atomic numbers but has also presented the discovery of some of the more important isotopes.

The addition of a summarizing table of the elements, of their discoverers, and the dates of discovery, such as Professor W. Muhlemann of Hamline University brought out through the Fisher Scientific Company in 1936, would be a very useful addition in future editions of the present work.

S. C. LIND.

Semi-conductors and Metals. By A. H. WILSON. 120 pp. New York: The Macmillan Company, 1939. Cambridge: University Press, 1939. Price: unbound, \$2.00.

This is one of the series of Cambridge Physical Tracts. The author needs no introduction to physicists and physical chemists.

The present tract is a most timely treatment of the electronic theory, metals, and semi-conduction. Naturally it deals with the various properties that can be described in terms of electronic behavior, such as thermal and magnetic properties and conductivity. This treatment is simple and non-mathematical. Full references are made to the literature of this field. The work is indispensable to one who wishes an introduction to the most modern work on the physical properties of metals.

S. C. LIND.

The Elements of Fractional Distillation. By CLARK S. ROBINSON AND EDWIN RICHARD GILLILAND. 8 x 6 in., xii + 267 pp.; 97 figures. New York: McGraw-Hill Book Company, 1939. Price: \$3.00.

With the recent advances in the treatment of the more complex distillation problems of industry, there was need of extension and revision of the two earlier editions of this book (1922 and 1930). The present revision is in collaboration with E. R. Gilliland.

As stated in the preface of the earlier editions, the authors attempt to give an introduction to the study of fractional distillation according to the best ideas of physical chemistry and chemical engineering. They specifically state that it is not

a complete treatise on the subject. The first part of the book discusses the phase rule in relation to simple and complex systems, followed by a discussion of the gas laws and solutions. This part of the book is essentially unchanged. For the purpose of the book, the treatment given in this part is probably adequate, but for a fundamental treatment according to the "best" modern ideas of physical chemistry, some improvement could be made as to completeness and correctness.

There has been a rearrangement and addition of new material in the latter part of the book. Chapters on special cases such as the distillation of ammonia, benzolized wash oil, methyl alcohol, and ethyl alcohol follow the short chapter on simple distillation and partial condensation, whereas in the earlier editions they were treated in the last part of the book along with chapters on rectification of the complex hydrocarbons.

There is a new chapter on binary mixtures in which the methods of Sorel, McCabe and Thiele, Ponchon, Savarit, Lewis, Smoker, and Fenske are discussed. The new chapter on multicomponent rectification is treated according to the work of Lewis and Matheson, Lewis and Cope, Underwood, and Brown and his associates. Other new chapters are on the rectification of adsorption naphtha and on column performance on the basis of plate efficiency, pressure drop, allowable rates of flow, etc. This is a worthwhile addition to the previous chapters on condensers and accessories.

The book is best suited to those interested in the elementary theory of distillation and the design of distilling apparatus for different purposes. It gives very little on the actual practical operation or installation of distillation equipment. The treatment of packed columns and the advantages, costs, and efficiency of various types of packing is too short; description or reference to certain types of packings and new columns has been omitted, as, for example, the centrifugal types.

The authors have advantageously added references at the end of many of the chapters and worked out a number of new problems, all of which makes the book more valuable. The rather extensive tables of data on various volatile liquids have been omitted, since it was felt that such data may be obtained from handbooks now available.

In an elementary treatise it would seem that the authors might well attempt to define more carefully all the new terms introduced as well as explain more fully the significance and units of their symbols. There are a number of annoying errors in labelling figures and following the labelling correctly in the text. As an example one may cite the description of figure 10 on page 22, where the primes are left off the letters in the discussion. Again, on page 39 they refer to the "dotted line AC" which is not dotted in the figure, an error carried over from the earlier edition. Most of the figures are fairly well chosen, but the units are often left off the diagrams and are sometimes hard to find in the text. While corrections of many of the mistakes and typographical errors, as well as some corrections in English, have been made in this new edition, some still remain. In general the book is written lucidly, but occasionally there is a poor choice of words which leaves the exact meaning obscure, especially for an elementary treatise. The generalizations in chapter XIV are illuminating. They would be of more value, however, if some attempt at a quantitative statement were also included.

T. I. TAYLOR.

Colloidal Phenomena. By ERNST A. HAUSER. First edition. 6 x 9 in.; xx + 294 pp.; 123 figures. New York: McGraw-Hill Book Company, 1939. Price: \$3.00.

This book can be strongly recommended as an introduction to colloid science. It is written in a lively style, without hesitation; simple curves and diagrams are

given in good number and often "one picture says more than many words". The first historical chapter contains a series of little-known and interesting facts.

Naturally opinions will differ as to the material that should be included in a book having this goal; the reviewer would miss gladly a good deal of the systematics brought in in the first chapters and would prefer to find, instead, in later ones more about solvation, coacervation, colloidal electrolytes, and Liesegang's rings. But the material chosen by Hauser is suitable for informing the reader as to the scope, the problems, the methods, and the results of colloid science.

The author avoids mathematical reasoning in the seventeen chapters, i.e., in two hundred and twenty-six pages of the book; he adds, however, an appendix of forty-six pages, containing a detailed mathematical discussion of some important colloidal problems. A certain preponderance given to the applications of optics and x-rays in colloidal physics is justified by their great significance.

H. FREUNDLICH.

First Report on Viscosity and Plasticity. Prepared by the Committee for the Study of Viscosity of the Academy of Sciences at Amsterdam. Second edition, 7½ x 10½ in.; viii + 272 pp.; 98 figures. New York: Nordemann Publishing Company, Inc. Price: \$7.00.

The First Edition of this First Report on Viscosity and Plasticity was reviewed briefly, together with the Second Report, a short time ago (*J. Phys. Chem.* **42**, 1249 (1938)). The fact that the second edition has been published after only four years proves how welcome this sound and extensive treatment of viscosity and plasticity has been to many readers.

The chapters particularly interesting to the physical chemist are the first and second ones by J. M. Burgers, entitled "Mechanical Considerations—Model Systems—Phenomenological Theories of Relaxation and Viscosity" and "Remarks in Connection with the Experimental Investigation of Flow Properties"; the third one, by H. G. Bungenberg de Jong, entitled "Viscosity Measurements with Special Reference to their Application in Colloid Chemistry"; the fourth one, by C. J. van Nieuwenburg, entitled "Viscosity and Plasticity from a Technical Point of View." The title of the third chapter might be misunderstood; it treats only the true, Newtonian viscosity of colloidal solutions, not their anomalous or structural viscosity. Anomalous viscosity has so far not been dealt with comprehensively in these reports, although many factors connected with it, e.g., yield value, plastometers, and the motion of small elongated particles in viscous liquids have been discussed in other chapters, for instance, in chapters I and IV of this First Report and in chapters III, IV, and V of the Second Report. Nevertheless, a special treatment of these phenomena, particularly as to their importance in colloid science, would be desirable.

The book under review is mainly an impression of the first edition. Minor changes are an interesting insertion in H. J. Jordan's chapter ("Viscosity Effects in Living Protoplasm") and an index.

H. FREUNDLICH.

Protective Coatings for Metals. By R. M. BURNS AND A. E. SCHUH. American Chemical Society Monograph No. 79. 407 pp.; 46 tables; 89 figures. New York: The Reinhold Publishing Corporation, 1939. Price: \$6.50.

This book is in a sense a revision of the monograph by H. S. Rawdon, published in 1927, but is enlarged to include protective coatings of all types, including paints and lacquers.

The subject matter of the book has been well selected, and throughout there is evidenced the thorough familiarity of the authorities with the methods of preparing

coatings, the methods of testing coatings, and the quality of coatings produced by various procedures. The book is unusually well written and is remarkably free from error.

The book is profusely illustrated with tables, data, curves, and micrographs. Literature references given in the form of footnotes, while not exhaustive, are well chosen and are adequate, so that the reader may inform himself in greater detail on any portion of the subject matter by reading these well-selected references. The reaction of this reviewer is well expressed by a portion of the foreword written by H. S. Rawdon, which reads as follows: "The investigator of the abstruse problems of corrosion, as well as the materials engineer seeking practical help in combating this problem by preventing corrosion by protecting the surface, will find this volume a veritable mine of information on all phases of the subject."

EDWIN M. BAKER.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 27: Magnesium. Teil B, Lieferung 4. 26 x 18 cm.; pp. 423-549. Berlin: Verlag Chemie, 1939. Price: 18.75 RM.

This section contains the conclusion of the description of the compounds of magnesium, mostly double salts with salts of alkali metals and including such analytically important substances as magnesium ammonium phosphate. This part contains a large number of phase rule diagrams. The section at the end deals with the technical preparation of magnesium compounds from various raw materials. The present part completes the B section on magnesium. The abundant numerical data make this a very useful section of the *Handbuch*.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 35. Aluminium. Teil A, Lieferung 6. 26 x 18 cm.; pp. 887-1110. Berlin: Verlag Chemie, 1939. Price: 27.75 RM.

This section deals with the alloys of aluminum with the metals from manganese to rhenium, inclusive, in the schematic order of *Gmelin*. The physical and chemical properties of the alloys and their analysis are dealt with, and the information is remarkably complete, the mechanical properties, for example, being fully dealt with. The text is very well illustrated with curves and diagrams, and there are many detailed tables of properties. The section will be of special interest to metallurgists as well as to chemists.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 68: Platin. Teil B, Lieferung 1. 26 x 18 cm.; pp. 1-72. Berlin: Verlag Chemie, 1939. Price: 8.25 RM.

This section deals with the physical properties of platinum under the following headings: nucleus, atom, crystallographic properties, mechanical properties, and thermal properties. Further sections continuing this description will follow. The literature is exhaustively covered, and some valuable pieces of information have been added from private unpublished sources. There is a section on the atomic weight of platinum, and one on the passage of gases through platinum. Since the physical properties of platinum are of importance in many branches of investigation, this section of *Gmelin* will be of very general interest.

J. R. PARTINGTON.

Lehrbuch der anorganischen Chemie. By ERNST H. RIESENFELD. Zweite, neubearbeitete Auflage. 7 x 10 in.; vii + 706 pp. Wien; F. Deuticke, 1939. Price: unbound, 10.50 RM.; bound, 12 RM.

When a book of this type calls for a second edition within five years, it is evidence of a favorable reception. In the meantime the author has gone from the University of Berlin to the Nobel Institute in Stockholm. The greatest value of this book lies in giving a comprehensive view of the whole field of chemistry, both descriptive and theoretical, necessarily condensed, but yet clear. It is such a book as should be required in the reading of every candidate for an advanced degree in chemistry, to furnish a true background for specialized work. I know of no other book which so well fills this place, the next best being Morgan and Burstall's *Inorganic Chemistry* (which should also be required), but Riesenfeld's book is not confined to modern developments and is broader, though of course, since it covers so much more ground, it is not as detailed. Another advantage to the American student is that its perusal would give a familiarity with the German vocabulary of chemistry, which would facilitate the reading of all German chemical literature.

New to this edition is the following: the chapter on "Isomerie und Isotopie bei Wasserstoff, Sauerstoff, und Wasser"; material on deuterium; the use of natural and artificial radioactive isotopes in solving problems of constitution; and the significant biochemical relations of many elements. Much other material is brought well up to date.

The theoretical material of physical chemistry is taken up in a natural connection, a subject often being treated at first in a simpler form; e.g., *catalysis* is first taken up under the combustion of hydrogen and carbon, then in connection with mass action and equilibrium, then under contact sulfuric acid, and finally under the Haber process; *complex salts* are first considered under nitrogen and ammonia in the amines and cyanides of nickel, then under nitric acid in connection with the coördination theory, then under the iron cyanides, and then very fully under the complex salts of chromium. Colloid chemistry is taken up under sulfur, and is excellently epitomized.

The historical data are rather carefully checked, and the industrial side, including metallurgy, is for the most part the practice of today. A few American developments have escaped notice: no mention is made of "HTH" or "TSP"; Pyrex glass is spoken of as "englisch"; the use of platinum in "Zahntechnik" is mentioned, but not that of palladium; of the electrolytic diaphragm cells, only the Griesheim and Billiton are referred to. But these are minor flaws and there are not many of them. A few illustrative experiments are described with good diagrams. The press-work leaves nothing to be desired, and only a very few typographical errors have been noticed (185.8° for -185.8° as the boiling point of argon, and so for krypton and xenon). Altogether, it is a comprehensive, well-balanced book, and one to be highly commended.

JAS. LEWIS HOWE.

THE CONSTITUTION OF THE ALLEGED "THIESSEN HYDRATES"¹

HARRY B. WEISER, W. O. MILLIGAN, AND W. J. COPPOC

Department of Chemistry, The Rice Institute, Houston, Texas

Received August 1, 1939

The slow hydrolysis of the ethylates of ferric iron, tin, and silicon yields highly hydrous precipitates of the respective oxides, which are almost amorphous to x-rays. Thiessen and coworkers (10, 11, 12, 13, 14, 15, 16, 17) have subjected these oxides to isothermal and isobaric dehydration and have obtained curves which indicate the existence of a series of definite hydrates stable over limited ranges of temperature and pressure. To illustrate: (a) iron oxide gel from ferric ethylate was said to give the hydrates $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, where $x = 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0$, and 0.5 ; (b) stannic oxide gel from stannic ethylate was said to form $\text{SnO}_2 \cdot x\text{H}_2\text{O}$, where $x = 2.5, 2.0, 1.75, 1.5, 1.0$, and 0.5 ; and (c) silica gel from ethyl silicate was said to yield the hydrates $\text{SiO}_2 \cdot x\text{H}_2\text{O}$, where $x = 3.0, 2.5, 2.0, 1.5, 1.0$, and 0.5 . Typical curves recently reported by Spychalski (8) for a silica sample from Thiessen's laboratory are reproduced in figure 1. At first glance such evidence of hydrate formation appears quite conclusive. Indeed, Hüttig and Fricke in their book, *Oxidehydrate und Hydroxide*, have devoted several pages to these unusual series of oxide hydrates and have dignified them by the name "Thiessen hydrates." In many years' experience (cf. 20) with the dehydration of gelatinous oxide hydrates and other dispersed systems, the authors failed to obtain sharp-step dehydration curves. Moreover, to the authors' knowledge no such curves of highly dispersed hydrates have been obtained by anyone except Thiessen and coworkers. On the contrary, in the dehydration of minutely crystalline or amorphous systems, all investigators except Thiessen have obtained smooth curves or curves with rounded steps only. For this and other reasons, the authors (21, 22, 23, 24) were led to question the individuality of the remarkable series of hydrates reported by Thiessen. Isothermal dehydration studies on hydrous ferric oxide from ferric ethylate, reported in 1935 (22), failed to indicate the presence of a single hydrate of the oxide. Thiessen and Koppen attributed our failure to find any ferric oxide hydrates to impurities in the sample and to faulty technique.

¹ Presented at the Sixteenth Colloid Symposium, held at Stanford University, California, July 6-8, 1939.

With reference to the latter, it was claimed that we waited so long for equilibrium to be established that the alleged hydrates, being somewhat unstable, decomposed during the time required to establish points on the curve. The first objection might have some validity, since we did not crystallize the solution of ferric ethylate that was hydrolyzed. The second objection does not appear to be valid, since the time required to obtain the points was similar in Thiessen's experiments and our own. Thiessen waited 15 min. after equilibrium was established, whereas we found that an approximate state of equilibrium was obtained in a half-hour at low temperatures, and readings were taken only after the pressure had remained approximately fixed for a half-hour. A much more significant difference (not mentioned by Thiessen) between the two sets of experiments was the fact that Thiessen's iron oxide was prepared at

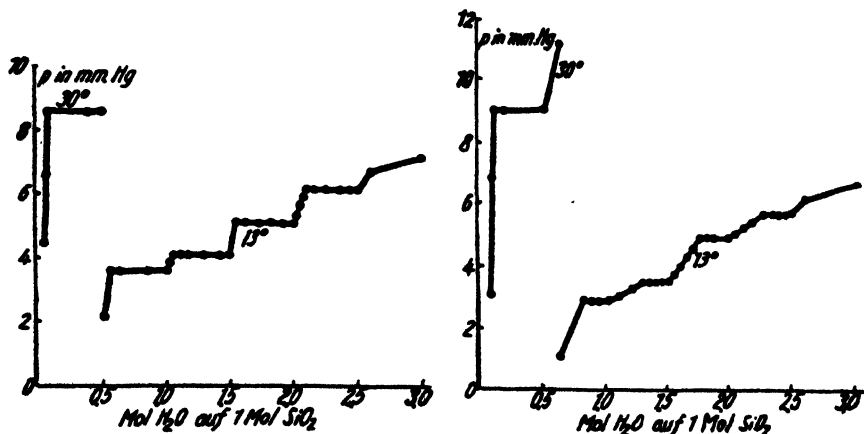


FIG. 1. Dehydration isotherms for hydrous silica from the hydrolysis of ethyl silicate (after Spsychalski)

approximately 17°C., whereas we carried out the hydrolysis at 25–30°C. It would be expected that any hydrates decomposing below 30°C. would have been missed in our experiments.

Because of the disagreement in the results, a comprehensive study was made of the alleged Thiessen hydrates of iron, tin, and silica, the utmost care being exercised in the preparation and dehydration of the samples.

EXPERIMENTAL

Apparatus and general procedure for isothermal dehydration

The isothermal dehydration of the oxide preparations was carried out in the apparatus shown diagrammatically in figure 2 (22, 24). The general procedure consisted in pumping off a definite amount of water and measuring the vapor pressure by means of a manometer filled with "vacuum

pump oil" of known density. Since hydrous ferric oxide tends to bump during dehydration (15), this preparation was placed in tube A (figure 2) and a mat of dried glass wool was placed above the sample to prevent loss in the event of bumping. The change in composition was followed by direct weighing. With all the other samples, the change in composition was followed by means of the McBain-Bakr balance (5, 19). The use of this device improved the experimental technique, since the apparatus did not have to be disconnected at any time during the running of a complete set of isotherms.

With highly hydrous bodies such as these under consideration, an approximate state of equilibrium is attained in a relatively short time at each pressure, especially at the low temperatures. Equilibrium was assumed to be established when the manometer showed no measurable

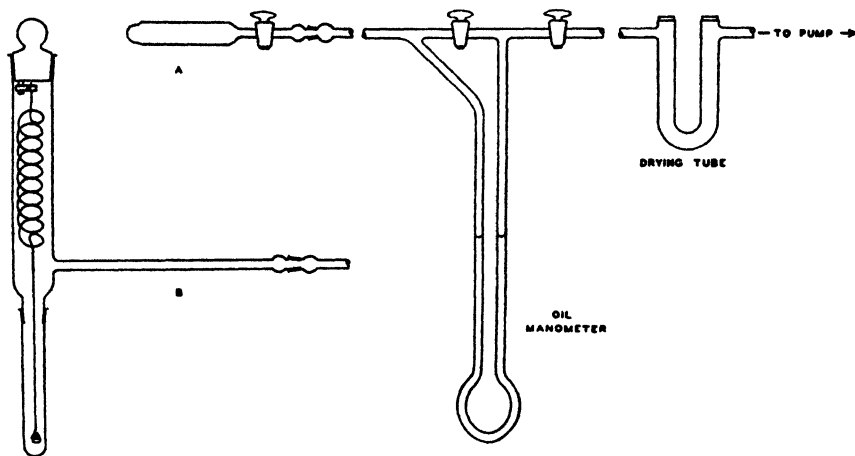


FIG. 2. Isothermal dehydration apparatus

increase in pressure in 15 min., that is, when the increase in pressure was less than 0.1 mm. of oil in 15 min. This required about 2 hr. at temperatures below 120–150°C.

For each isotherm, temperatures were maintained constant to 0.05°C. in either a water or an oil thermostat, depending on the temperature. Changes in vapor pressure and in the length of the silica spring were measured with precision measuring microscopes. The oil manometer was immersed in a thermostat at 25°C. For minute details of procedure the reader is referred to the Doctorate Thesis of Mr. W. J. Coppoc, copies of which are available in the library of The Rice Institute.

Hydrous ferric oxide

Preparation of samples. Ferric ethylate was prepared by the interaction of solutions of anhydrous ferric chloride and sodium ethylate in

absolute alcohol. The procedure was carried out in an apparatus similar to that of Thiessen and coworkers (10, 11, 12, 13, 14, 15, 16, 17), except that the following special precautions were taken to secure a highly pure product: (a) All materials were protected from atmospheric moisture with dry-air trains consisting of calcium chloride, magnesium perchlorate trihydrate, and phosphorus pentoxide. The absolute alcohol was prepared by distilling commercial absolute alcohol from metallic calcium, followed by further drying by the method of Smith (7), to give a product that contained less than 0.1 per cent of water. The ferric chloride was Baker and Adamson anhydrous salt, which was resublimed before dissolving in the special absolute alcohol, using a "dry-air box" to effect the transfer. The sodium ethylate was prepared by placing a definite amount of pure sodium in a reaction flask and covering it with absolute alcohol made as described above. These operations were carried out in an atmosphere of dry hydrogen in a dry box.

After the interaction between sodium and alcohol was complete, an exactly equivalent amount of the ferric chloride solution was run in. The reaction mixture was refluxed for 24 hr. and allowed to stand until the sodium chloride had settled out, after which the supernatant ferric ethylate solution was drawn into a dry flask through a filter of fritted glass. This flask was sealed tightly to prevent even a trace of moisture from entering and was allowed to stand for several weeks until a crop of ferric ethylate crystals were formed. The crystals were large, well-defined, and dark brown in color.

Sutra (9) failed to get pure crystals of ferric ethylate, probably because he worked with too dilute solutions or did not maintain the solution dry for a sufficient length of time. In the experiments described above approximately 30 g. of ferric chloride in 1500 cc. of special absolute alcohol were employed. Crystals of ferric ethylate separate much more quickly if the concentrations of the solutions of ferric chloride and sodium ethylate are doubled. Under these conditions the temperature of the mixture must be maintained just below the boiling point until the filtration is complete, after which the ferric ethylate solution may be cooled slowly to 8°C. and allowed to stand at that temperature. A crop of crystals separates within 2 or 3 days.

Crystals obtained as above described were removed from the supernatant liquid, washed with the special alcohol, and then dissolved in 500 cc. of this alcohol. After analysis for iron content, an amount necessary to give a final concentration which was 15 millimolar with respect to ferric oxide was diluted to 1000 cc. with the special absolute alcohol. This solution in a 2-liter unstoppered Erlenmeyer flask was placed in a thermostat at 17°C., and moisture from the air was allowed to diffuse in and hydrolyze the ferric ethylate. The reaction was complete in approxi-

mately 4 weeks, after which time the resulting hydrous ferric oxide was collected, washed with 95 per cent alcohol, and dried to a composition of

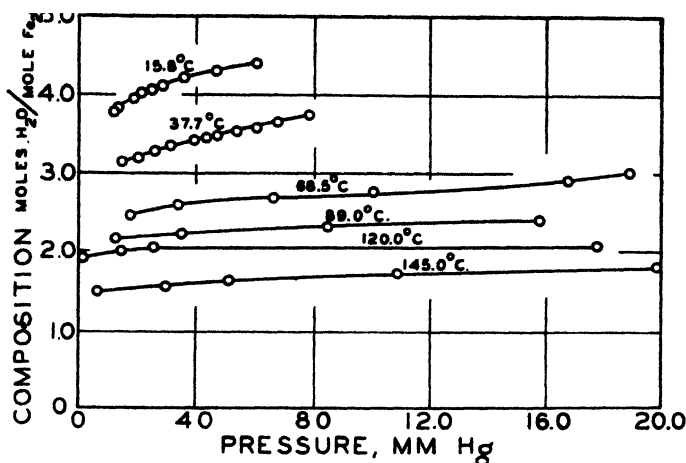


Fig. 3. Dehydration isotherms for hydrous ferric oxide from slowly crystallized ferric ethylate

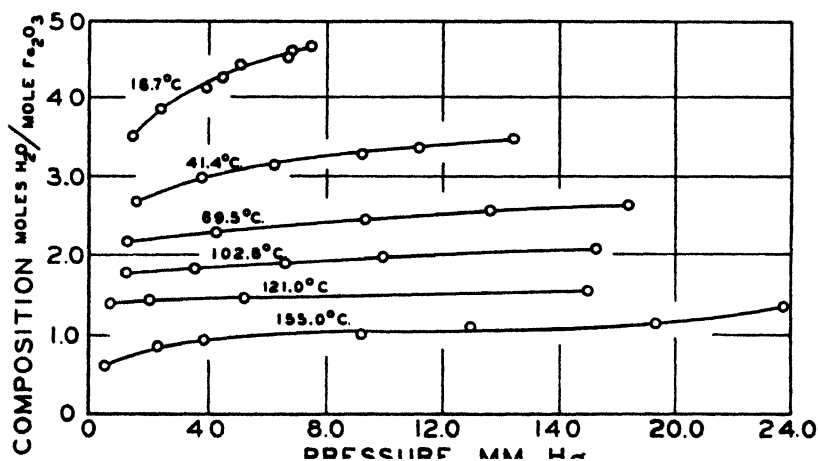


Fig. 4. Dehydration isotherms for hydrous ferric oxide from slowly crystallized ferric ethylate

about 5.5 moles of water per mole of ferric oxide. At no time was the temperature allowed to rise above ca. 17°C.

Isothermal dehydration. Three distinct samples of ferric oxide were dehydrated isothermally. The results are shown in figures 3, 4, and 5. Samples I and II were prepared by hydrolysis of ferric ethylate which had

separated very slowly from a weakly supersaturated solution of the salt. Sample III, prepared a year later, was obtained from the ethylate precipitated more rapidly from the more highly supersaturated solution.

An approximate state of equilibrium was attained in *ca.* 2 hr. at each pressure for the lower temperatures, but at 155°C. the pressure was found to be increasing somewhat at the end of 2 hr. This was traced to a slow transformation of the oxide, amorphous to x-rays, to definitely crystalline $\alpha\text{-Fe}_2\text{O}_3$ (hematite), possessing a distinctly different color. This spontaneous transformation is known to go on very slowly at low temperatures in contact with water (22), so that a state of *absolute* equilibrium is never attained in a reasonable time at any temperature.

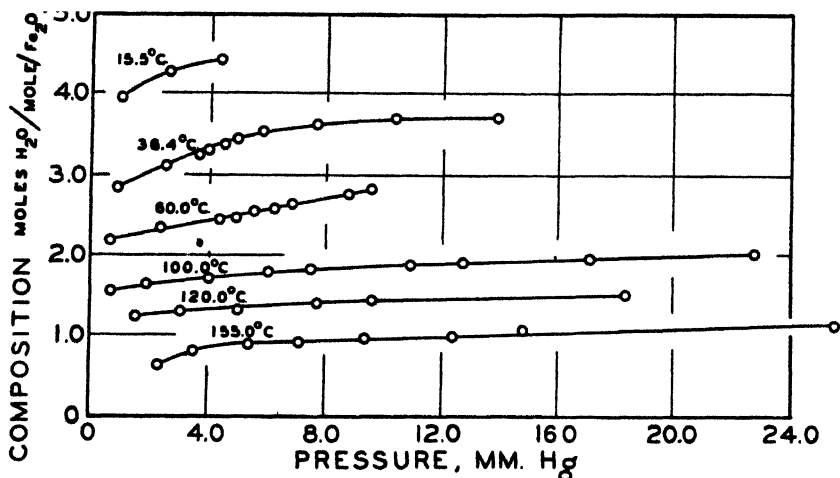


FIG. 5. Dehydration isotherms for hydrous ferric oxide from rapidly crystallized ferric ethylate

The results in figures 3, 4, and 5 give no indication whatsoever of the existence of hydrates of ferric oxide. These observations with the oxide, prepared especially pure under carefully controlled conditions both of formation and of dehydration, confirm our earlier conclusions (21, 22, 23) that the hydrates claimed by Thiessen have no existence in fact. Thiessen contends that we missed the hydrates because they were transient and we failed to catch them "on the run." This contention is not justified, because equilibrium was attained fairly promptly at the low temperatures, and a series of isotherms once started was completed without interruption. Moreover, in special experiments which were carried out to determine the rate at which equilibrium was set up at various temperatures, we failed to detect any indications of the unstable hydrates assumed by Thiessen.

Hydrous stannic oxide

Preparation of samples. Stannic ethylate was prepared and hydrolyzed in essentially the same way as ferric ethylate. Stannic ethylate differs from the iron salt in crystallizing from absolute alcohol much more easily and rapidly. The samples of ethylate were recrystallized five times before subjecting their dilute alcoholic solution to slow hydrolysis.

Isothermal dehydration. Two samples of hydrous stannic oxide were subjected to isothermal dehydration. The first sample, obtained after several weeks' hydrolysis, was washed with 95 per cent alcohol and dried, first between filter papers and then with a vacuum pump to a composition approximately $\text{SnO}_2 \cdot 5\text{H}_2\text{O}$. This sample, when subjected to isothermal dehydration, gave the curves shown in figure 6. Referring to the 15°C .

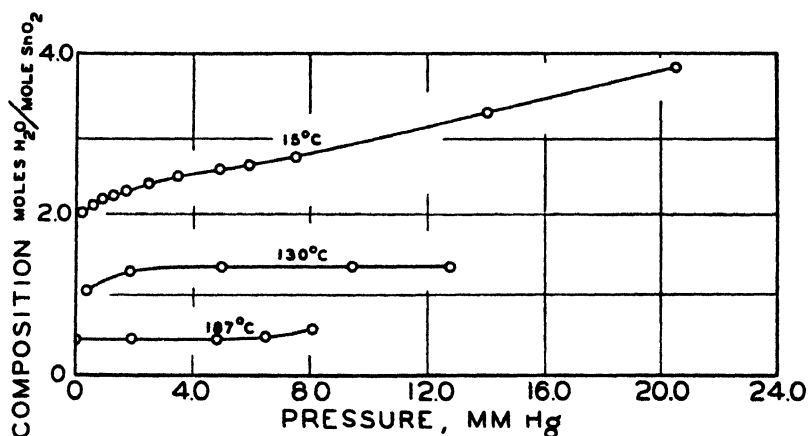


FIG. 6. Dehydration isotherms for hydrous stannic oxide dried between filter papers and with a vacuum pump

isotherm, it will be noted that the sample gives an abnormally high vapor pressure (even above that of water at this temperature). Since the odor of alcohol was detectable over the sample, it was assumed that adsorbed alcohol accounted for the high vapor pressure.

The second sample was exposed to the atmosphere at 17°C . for 2 weeks before subjecting it to isothermal dehydration, data for which are shown graphically in figure 7. The lower initial vapor pressure of this sample at 15°C . shows that excess alcohol either evaporated, or upon exposure to air was displaced by water adsorbed from the atmosphere. It is of interest that the original 11°C . isotherm of Thiessen and Koerner (13) for stannic oxide likewise showed an abnormal vapor pressure, but that later 11°C . isotherms for the same sample exhibited a decreasing abnormality. Thies-

sen claimed that his sample contained no alcohol, in spite of this evidence to the contrary.

Figures 6 and 7 fail to give any evidence of hydrate formation. This confirms the results of our earlier isobaric dehydration and x-ray diffraction studies (21) on the oxide from stannic ethylate. It appears, therefore, that stannic oxide gel precipitated by any known method consists of minute crystals of anhydrous SnO_2 (cassiterite) with adsorbed and entrained water.

Hydrous silica from ethyl silicate

Preparation of samples. Hydrous silica was formed by the hydrolysis of pure, redistilled ethyl silicate. Two samples of the oxide were prepared, one in the spring of 1938 and the second in the fall and winter of 1938–39.

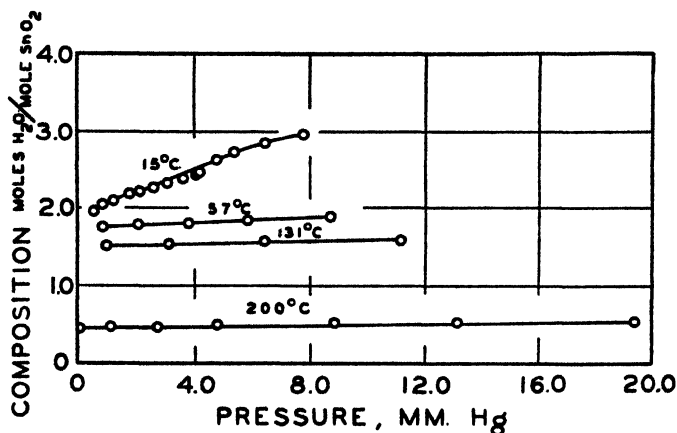


FIG. 7. Dehydration isotherms for hydrous stannic oxide dried in air at 17°C.

Both samples were made by using 37 cc. of ester, 18.5 cc. of absolute alcohol, and 1850 cc. of distilled water in a 4-liter Erlenmeyer flask. The flask was shaken vigorously, placed in a thermostat, and the contents stirred mechanically for 4 days. On standing quietly for 2.5 months, a copious gel resulted. The supernatant liquid was poured off, and excess liquid was removed by breaking the gel and centrifuging the resulting suspension. One part of sample I was dried rapidly to approximately $\text{SiO}_2 \cdot 10\text{H}_2\text{O}$, using first a water pump and then a Cenco Hyvac pump. Duplicate isotherms at 10.5°C. of one portion of sample I were obtained in June, 1938 (figure 8, curves A and B). A second portion of sample I was dried as above described and was stored in a mechanical refrigerator at approximately 8°C. for 7 months, after which time duplicate 11.6°C. isotherms were obtained (figure 9, curves B and D). A third portion of sample I was stored in contact with liquid water at 8°C. for 9 months, and

was then subjected to isothermal dehydration. The 11.6°C. isotherm shown in figure 9, curve A, was obtained for the aged portion of sample I after drying between filter papers. Curve C of figure 9 is the 11.6°C. isotherm for the 9 months' old sample I after washing five times with water, five times with alcohol, and five times with water, and drying between filter papers.

Sample II was dried between filter papers and with the vacuum pump to a composition of approximately $\text{SiO}_2 \cdot 10\text{H}_2\text{O}$ and was stored at 8°C.

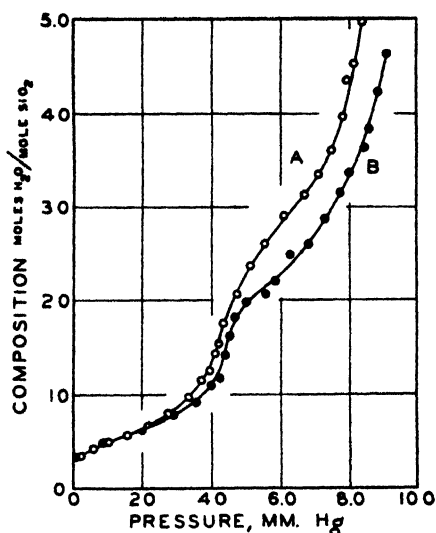


FIG. 8

FIG. 8. Dehydration isotherms (10.5°C.) for hydrous silica. Sample I, dried with a water pump and vacuum pump, and used at once. A and B are duplicate isotherms.

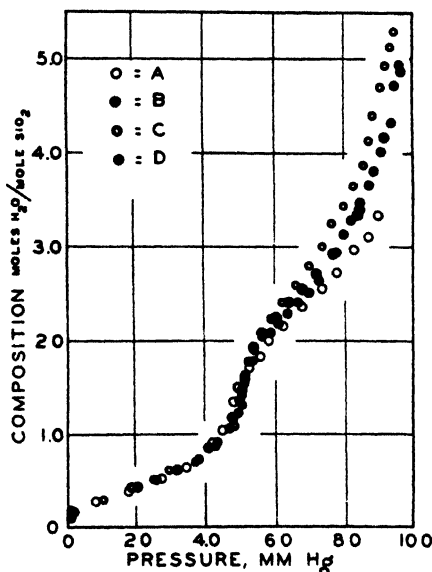


FIG. 9

FIG. 9. Dehydration isotherms (11.6°C.) for hydrous silica. Sample I: curves B and D are duplicate isotherms for silica dried with a water pump and a vacuum pump, and aged at 8°C. for 7 months. (A) Sample dried between filter papers and aged at 8°C. for 9 months. (C) Sample washed with water, alcohol, and water, and dried between filter papers.

until used. Duplicate isotherms at 11.6°C. are shown in figure 10, curves A and B.

It is apparent that the dehydration curves give no indication of the existence of the series of silica hydrates reported by Thiessen and co-workers. Unlike the dehydration curves for the hydrous oxides from the ethylates of iron and tin, the curves for hydrous silica from ethyl silicate show one point of inflection, the position of which varies somewhat with

different samples. This could be due to a definite hydrous hydrate such as $\text{SiO}_2 \cdot \text{H}_2\text{O}$, but the evidence is by no means conclusive. In his classical work on the dehydration of silica, van Bemmelen (18) observed a point of inflection in the dehydration curves. This was confirmed by Zsigmondy, Bachman and Stevenson (25), Anderson (1), Bachman (2), Lenher (4), Berl and Urban (3), and others (20). A possible explanation is that two kinds of adsorption are involved: (1) capillary condensation in the pores of the gel structure and (2) monomolecular adsorption on the silica surface that constitutes the walls of the capillaries (6). In the event that the loss

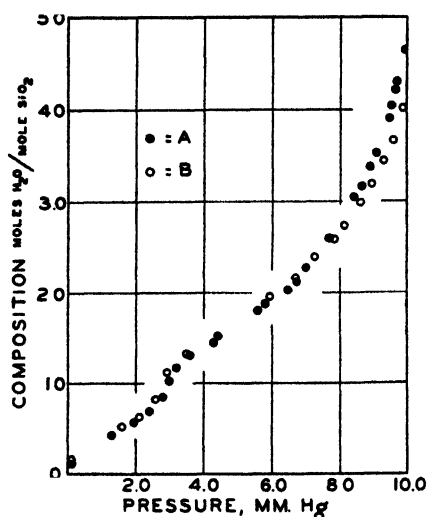


FIG. 10

FIG. 10. Dehydration isotherms (11.6°C.) for hydrous silica. Sample II, dried between filter papers and used at once. A and B are duplicate isotherms.

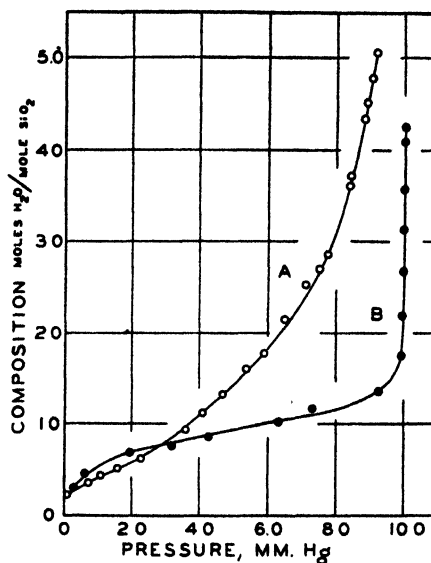


FIG. 11

FIG. 11. Dehydration isotherms (11.6°C.) for hydrous silica from sodium metasilicate. (A) Sample III, precipitated at room temperature and dried with a vacuum pump. (B) Sample IV, precipitated at 0°C. and dried between filter papers.

of water from capillaries takes place almost completely before desorption from the surface begins, the isothermal dehydration curve will show a point of inflection on passing from one type of adsorption to the other. This would explain why the point of inflection will vary with different samples. On the other hand, if desorption from capillaries and from the surface takes place simultaneously in the critical range, the dehydration isotherm for the same system considered above may show a slight point of inflection or no point of inflection. The variation in position and degree of the flection in the curves from different samples of hydrous silica from

ethyl silicate suggests that the changes of direction are due to what may be termed the van Bemmelen phenomenon, rather than to the loss of water from a definite hydrate of silica.

Hydrous silica from sodium metasilicate

Preparation of samples. Samples III and IV of silica were prepared by adding 30 cc. of glacial acetic acid to a solution containing 50 g. of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ in 125 cc. of water. In preparing sample III the solutions were mixed at room temperature, and in preparing sample IV the solutions were cooled to 0°C . before mixing so that the temperature never rose above 20°C . The samples were washed until the wash water was neutral to litmus. Sample III was dried by use of a vacuum pump, and sample IV was dried between filter papers.

Isothermal dehydration. The two samples prepared as above described were dehydrated isothermally at 11.6°C . with the results shown graphically in figure 11. Curve A was obtained from the sample precipitated at room temperature, and curve B from the sample formed at 0°C .

The perpendicular portion of curve B represents the vapor pressure of water at that temperature. Neither curve shows a point of inflection like those in figures 8 and 9 and (to a much smaller extent) in figure 10. Moreover, they differ from the curves of van Bemmelen and Anderson in showing no point of inflection. These differences might be expected, since the conditions of preparation vary widely. The freshly formed gel from sodium metasilicate was precipitated rapidly and was not allowed to age. The gels from ethyl silicate were formed slowly, and therefore should possess a physical structure different from that of the gels from the metasilicate. The aged gels from ethyl silicate give a more pronounced point of inflection (figure 9) than the fresh gels from ethyl silicate (figures 8 and 10). Van Bemmelen's gels were prepared from silicate of soda solution containing colloidal silica that was as old as the water glass solution. A gel precipitated from sodium metasilicate and aged for several months might give a point of inflection similar to that obtained by van Bemmelen with the gel from water glass. This experiment will be carried out.

SUMMARY

The following is a brief summary of the results of this investigation:

1. Thiessen and coworkers have reported the preparation of ten definite hydrates of ferric oxide, six definite hydrates of stannic oxide, and six definite hydrates of silica. These series of alleged hydrates were detected by sharp steps in the dehydration isotherms of gels prepared by the slow hydrolysis of the ethylates of iron, tin, and silicon, respectively. The improbability that highly hydrous materials will give sharp-step dehydration isotherms has been pointed out.

2. The hydrous gels prepared by the slow hydrolysis at 15°C. of ferric, stannic, and silicon ethylates have been subjected to isothermal dehydration. The experimental technique was simplified and rendered more accurate by the use of the McBain-Bakr balance.

3. The dehydration isotherms for ferric oxide and stannic oxide prepared from the ethylates show no points of inflection that would indicate the presence of definite hydrates. These hydrous gels consist of the oxides with adsorbed or entrained water.

4. The dehydration isotherms for hydrous silica from the ethylate give one point of inflection, the position of which varies with the conditions of formation and treatment of the sample. This inflection point may correspond to a definite hydrate, such as $\text{SiO}_2 \cdot \text{H}_2\text{O}$, but the evidence is not conclusive. There is no indication of the series of hydrates claimed by Thiessen and coworkers.

5. The dehydration isotherms for samples of hydrous silica prepared at 0°C. and at room temperature, by the interaction of solutions of sodium metasilicate and acetic acid, show no indication of hydrate formation.

REFERENCES

- (1) ANDERSON: *Z. physik. Chem.* **88**, 191 (1914).
- (2) BACHMAN: Dissertation, Leipsig, 1913.
- (3) BERL AND URBAN: *Z. angew. Chem.* **36**, 57 (1925).
- (4) LENHER: *J. Am. Chem. Soc.* **43**, 391 (1921).
- (5) MCBAIN AND BAKR: *J. Am. Chem. Soc.* **48**, 690 (1926).
- (6) SEMENOFF: *Z. physik. Chem.* **37**, 471 (1930).
- (7) SMITH: *J. Chem. Soc.* **1927**, 1288.
- (8) SPYCHALSKI: *Z. anorg. Chem.* **239**, 317 (1938).
- (9) SUTRA: *Bull. soc. chim.* [4] **47**, 68 (1930).
- (10) THIESSEN AND KOERNER: *Z. anorg. Chem.* **180**, 65 (1929).
- (11) THIESSEN AND KOERNER: *Z. anorg. Chem.* **189**, 168, 174 (1930).
- (12) THIESSEN AND KOERNER: *Z. anorg. Chem.* **191**, 74 (1930).
- (13) THIESSEN AND KOERNER: *Z. anorg. Chem.* **195**, 83 (1931).
- (14) THIESSEN AND KOERNER: *Z. anorg. Chem.* **197**, 307 (1931).
- (15) THIESSEN AND KOPPEN: *Z. anorg. Chem.* **189**, 113 (1931).
- (16) THIESSEN AND KOPPEN: *Z. anorg. Chem.* **200**, 181 (1931).
- (17) THIESSEN AND KOPPEN: *Z. anorg. Chem.* **233**, 57 (1936).
- (18) VAN BEMMELN: *Die Absorption*. Theodor Steinkopff, Dresden (1910).
- (19) WEINHART: *Rev. Sci. Instruments* **4**, 350 (1933).
- (20) WEISER: *Inorganic Colloid Chemistry*. Vol. II, *The Hydrous Oxides and Hydroxides*. John Wiley and Sons, Inc., New York (1935).
- (21) WEISER AND MILLIGAN: *J. Phys. Chem.* **36**, 3030 (1932).
- (22) WEISER AND MILLIGAN: *J. Phys. Chem.* **39**, 25 (1935).
- (23) WEISER AND MILLIGAN: *Trans. Faraday Soc.* **32**, 358 (1936).
- (24) WEISER AND MILLIGAN: *Chem. Rev.* **25**, 1 (1939).
- (25) ZSIGMONDY, BACHMAN, AND STEVENSON: *Z. anorg. Chem.* **75**, 189 (1912).

THE EFFECTS OF CERTAIN SALT MIXTURES ON THE DISSOCIATION OF GLYCINE AND ALANINE^{1,2}

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Many papers, too numerous to mention here, have shown that the presence of neutral salts influences the ionization of weak electrolytes in aqueous solution. It has also been shown on numerous occasions that the effects of the salts can be quantitatively explained on the basis of the Debye-Hückel theory of interionic attraction. Amino acids differ from most of the less complex weak electrolytes by nature of the highly polar structure of the electrically neutral molecule. The electrostatic fields surrounding this highly polar molecule may be expected to be more intense than those surrounding the relatively non-polar molecules of weak electrolytes such as acetic acid and ammonia. However, it is also to be expected that, with suitable correction for the polarity of the amino acid molecules, the Debye-Hückel equation will be equally applicable to the effects of salts on the ionization of amino acids. The experiments of Sørensen (19), Neuberger (13, 14), Kawai (8), and Morton (12) are at least qualitatively in accord with this expectation.

In 1928 Simms (18) published some interesting observations on the effects of salt mixtures on the ionization of glycine. An "antagonism" between the effects of sodium or potassium and calcium or magnesium ions was noted. The biological phenomenon of "ion antagonism" is frequently regarded as being dependent in some manner on the surface area presented by the large particles of protoplasm and the cell membranes. The report of Simms was of interest, since it dealt with an example of "ion antagonism" that occurred in a single-phase system. It was of particular interest in its bearing on the general theory of electrolytes, because of the anomalous nature of the experimental results reported.

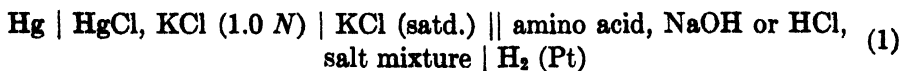
¹ Presented at the Sixteenth Colloid Symposium, held at Stanford University, California, July 6-8, 1939.

² This work was aided by grants from the Research Board of the University of California and from Eli Lilly and Company. The authors are indebted to the Cyrus K. Warren Fund of the American Academy of Arts and Sciences for the loan of the Type K potentiometer.

The present communication deals with the reinvestigation of certain parts of the work of Simms and an extension of it to include the effects of salt mixtures on the ionization of alanine.

EXPERIMENTAL TECHNIQUE

The results have been obtained by measurement of the E.M.F. of cells of the type



where the amino acid concentration was about 0.02 *M* and the salt concentrations were varied between wide limits.

Stock solutions of the amino acid and sodium hydroxide or hydrochloric acid were made up to twice the concentration that was desired in the experimental solutions. The salt whose concentration was to be maintained constant throughout the given series was added to the stock solution. The experimental solutions were made up by pipetting 12.5 cc. of the stock solution into 25-cc. volumetric flasks, adding the desired amounts of a stock solution of the salt whose concentration was to be varied throughout the series, and diluting to volume with distilled water. All salts and amino acids were purified by recrystallization.

The hydrogen electrode consisted of a short piece of platinum wire sealed through one end of a short length of glass tubing. The wire was coated with platinum black by electrolysis in the customary manner. The vessel for the hydrogen electrode was surrounded by a water jacket, through which water at 25.0°C. was circulated. The whole apparatus was kept in an air bath at 25.0°C. The calomel cell was prepared according to the directions of Clark (3). The hydrogen was prepared electrolytically. The E.M.F. was measured with a Leeds and Northrup Type K potentiometer in conjunction with a Leeds and Northrup Type 2420-c galvanometer. The standard cell was checked against one that was certified by the Bureau of Standards.

After the E.M.F. was corrected to 1 atmosphere pressure of hydrogen, the evaluation of the pH of the solutions was made with the aid of the table given by Schmidt and Hoagland (16).

RESULTS

As a preliminary to further investigation of the phenomena reported by Simms, several of his series were selected at random and repeated. All of the solutions were made up at the concentrations that are stated in his tables. The pH of the solutions was determined in the manner that is previously described.

The experimental results are presented graphically in figures 1 and 2. The points on the graphs are experimental and the curves were drawn to fit the points. The curves representing Simms' data have been drawn through all of his points and in the manner adopted by him. The lower curves in figure 1, with the experimental points marked by circles, show the effects of varying amounts of sodium chloride on the pH of a glycine buffer containing 0.01 *M* magnesium chloride. The upper curves in figure 1, marked by squares, illustrate the effects of sodium chloride on the pH of a glycine buffer containing 0.00416 *M* calcium chloride. The effects of calcium chloride on the pH of a glycine buffer containing 0.0025 *M* magnesium chloride are shown in figure 2.

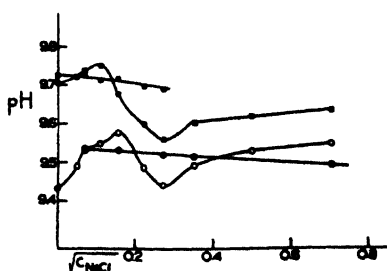


FIG. 1

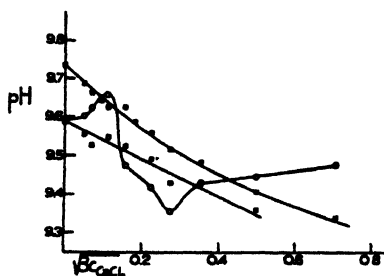


FIG. 2

FIG. 1. A comparison of the present results with those reported by Simms. Concentration of glycine, 0.10 *M*. 0.05 equivalent of sodium hydroxide added. Measurements with the hydrogen electrode. 0.00416 *M* calcium chloride, concentration of sodium chloride varied: ■, present data; □, data of Simms. 0.01 *M* magnesium chloride, concentration of sodium chloride varied: ●, present data; ○, data of Simms.

FIG. 2. A comparison of the present results with those of Simms. Concentration of glycine, 0.10 *M*. 0.5 equivalent of sodium hydroxide added. 0.0025 *M* magnesium chloride. Concentration of calcium chloride varied. ○, data of Simms; □, present data, measurements with the hydrogen electrode; ■, present data, measurements with the glass electrode.

It was felt that further evidence concerning the accuracy of Simms' observations should be obtained by the application of a second method; therefore certain experiments were carried out with the aid of a glass electrode. The vacuum-tube amplifier was of the type designed by DeEds (5). The glass electrode was of the bulb type, blown from Corning 015 glass. Temperature control was obtained by means of an air bath. The remainder of the apparatus was similar to that employed in connection with the hydrogen electrode.

The results of a series that is representative of those that were carried out with the aid of the glass electrode are shown in figure 2. Since the absolute values of the pH were of relatively small importance for the

present purpose, the glass electrode was standardized with a buffer whose pH was only approximately known. Any difference in the slopes of the two present curves may in all probability be explained by the influence of salts on the potential of the glass electrode (11).

The results presented above cast serious doubt on the validity of the observations of Simms. It is believed that the accuracy of the present experiments was sufficient to disclose any variations of the magnitude reported by Simms. However, it should be mentioned that at times variations of points from a smooth curve were observed. In no case did the variations agree with those of Simms. Because of this, and the failure to reproduce them, it is felt that there is sufficient justification for regarding these variations as the result of one of the many possible sources of experimental deviation in electrode technique. Also, it is believed that the similarity of the results obtained with the glass electrode to those obtained with the hydrogen electrode serves as further proof of the correctness of the present results.

No attempt to offer an explanation of the differences between the present results and those of Simms is made. In the absence of more detailed information concerning his experimental technique, any such attempt would be futile.

It should be pointed out that, on the basis of the present theory of electrolyte solutions, the effects of salts on the properties of the solute or on the colligative properties of the solution may be expected to be some simple function of the salt concentration. Thus, activity coefficients of uni-univalent salts have repeatedly been found to be proportional to the square root of the concentration in dilute solutions and to be expressible by an equation involving the square root of the concentration and the first power of the concentration in more concentrated solutions. Theoretical justification for these relationships has been found in the theory of electrostatic attraction between the ions. Any radical departure from these simple relationships, such as those noted by Simms, must be regarded as highly anomalous. It is therefore felt that the burden of the proof and explanation lies with the observer of the abnormal phenomena.

The effects of magnesium chloride, sodium chloride, barium chloride, and certain mixtures thereof on the ionization of alanine in acidic solutions are shown in figure 3. $-\log K'_A$ has been plotted as the abscissa, where $-\log K'_A$ is defined by

$$-\log K'_A = -\log \alpha_{H^+} - \log \frac{c_{R^{+-}}}{c_{R^+}} \quad (2)$$

By plotting this function, instead of pH, it has been possible to compare series that were made up to differing degrees of neutralization. $c_{R^{+-}}$ and c_{R^+} , respectively, represent the concentrations of the alanine zwitter ion

and the alanine cation. α_{H^+} represents the hydrogen-ion activity. The concentrations in the ratio in equation 2 have been evaluated by means of the expressions

$$\begin{aligned} c_{R^{+-}} &= c_T - c_A + c_{H^+} \\ c_{R^+} &= c_A - c_{H^+} \end{aligned} \quad (3)$$

where c_T represents the total concentration of amino acid, c_A the added concentration of hydrochloric acid, and c_{H^+} the hydrogen-ion concentra-

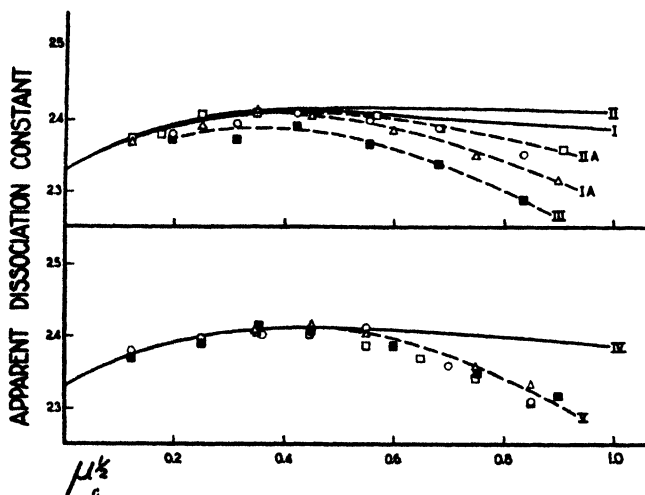


FIG. 3. The effects of sodium chloride, magnesium chloride, barium chloride, and their mixtures on the ionization of alanine in acidic solutions. Concentration of alanine, approximately 0.03 *M*. 0.5 equivalent of hydrochloric acid added. Upper half: Δ = concentration of magnesium chloride varied; \square = concentration of sodium chloride varied; \circ = 0.008 *M* magnesium chloride, concentration of sodium chloride varied; \blacksquare = 0.02375 *M* sodium chloride, concentration of magnesium chloride varied. Lower half: \blacksquare = concentration of magnesium chloride varied; \circ = concentration of barium chloride varied; \square = 0.03575 *M* magnesium chloride, concentration of barium chloride varied; Δ = 0.0358 *M* barium chloride, concentration of magnesium chloride varied. Curves I, II, and IV are theoretical.

tion. Because the values of the activity coefficient of neither hydrochloric acid nor the hydrogen ion in the salt mixtures are available, the *approximation* that the activity coefficient of the hydrogen ion equals unity has been made for the purpose of evaluating c_{H^+} in equation 3.

The ionic strength has been calculated in terms of moles per liter of solution and is denoted by μ_c . In this calculation, the concentration of that portion of the amino acid that is in its electrically neutral form has been neglected. All other ionic species in the solution have been included in the summation.

The solid lines in figure 3 have been calculated according to the theoretical equation

$$-\log K'_A = -\log K_A + \log \gamma_{R+-} - \log \gamma_{R+} \quad (4)$$

which is readily obtained from equation 2 by introduction of the expression $c\gamma = \alpha$, where γ represents the activity coefficient of the species denoted by the subscript. K_A is the thermodynamic dissociation constant and is defined by

$$K_A = \frac{\alpha_{H+}\alpha_{R+-}}{\alpha_{R+}} \quad (5)$$

Log γ_{R+} in equation 4 was calculated according to the Debye-Hückel (4) equation

$$-\log \gamma = \frac{0.504 \sqrt{\mu_c}}{1 + 0.328a \sqrt{\mu_c}} \quad (6)$$

TABLE 1

Values of R , b , a' , and a used in calculating solid curves in figure 3

	CURVES I AND IV	CURVE II
R (dipole distance), in Å.....	4.19	4.19
b (radius of zwitter ion), in Å.....	3.08	3.08
a' (Debye-Hückel), in Å.....	4.9	4.6
a (Kirkwood), in Å.....	4.65	5.0

in which a represents the "collision diameter" of the ions. Log γ_{R+-} was calculated by Kirkwood's (9) equation for the activity coefficients of zwitter ions.

The simplest assumption regarding the alanine zwitter ion is that the molecule may be represented as a sphere and that the center of the dipole corresponds to the center of the sphere. Upon consideration of a spatial model of alanine, it will be evident that the spherical conditions are reasonably well approximated. Under these conditions, all terms but the first one in the infinite summation of Kirkwood's equation are equal to zero. $-\log \gamma_{R+-}$ is therefore dependent on the dipole of the zwitter ion, the diameter of the molecule, and the "collision diameter," which is a factor analogous to the a in the Debye-Hückel equation.

The values used in the calculations of the solid curves in figure 3 are given in table 1. The values of the universal constants were obtained from Birge's (10) compilation.

The effects of salts and their mixtures on the ionization of alanine in basic solutions are shown in figures 4 to 8. $-\log K'_B$, which is defined by

$$-\log K'_B = -\log \alpha_{\text{OH}^-} - \log \frac{c_{\text{R}^{+-}}}{c_{\text{R}^-}} \quad (7)$$

has been plotted as the abscissa. α_{OH^-} represents the hydroxyl-ion activity, and c_{R^-} represents the concentration of the alanine anion. α_{OH^-} was determined from α_{H^+} by the expression

$$\alpha_{\text{H}^+} \alpha_{\text{OH}^-} = K_W \quad (8)$$

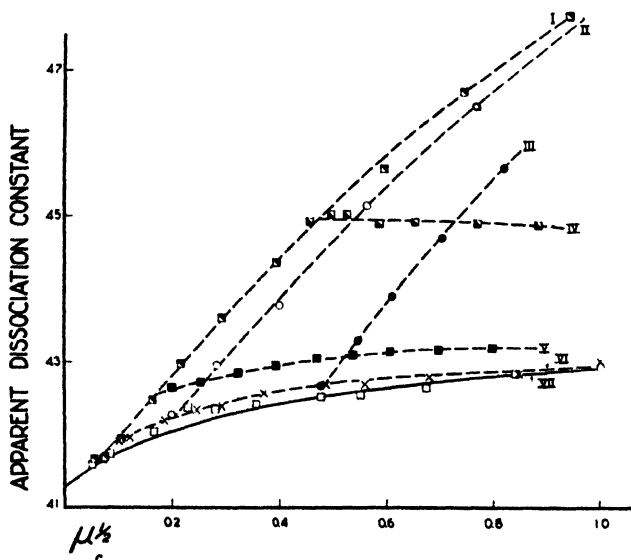


FIG. 4. The effects of magnesium chloride, sodium chloride, and their mixtures on the ionization of alanine in basic solutions. Concentration of alanine, approximately 0.03 *M*. Concentration of sodium hydroxide, 0.003 *M*. \square = concentration of magnesium chloride varied; \circ = 0.0375 *M* sodium chloride, concentration of magnesium chloride varied; \bullet = 0.225 *M* sodium chloride, concentration of magnesium chloride varied; \blacksquare = 0.0691 *M* magnesium chloride, concentration of sodium chloride varied; \blacksquare = 0.0125 *M* magnesium chloride, concentration of sodium chloride varied; \times = 0.0025 *M* magnesium chloride, concentration of sodium chloride varied; \square = concentration of sodium chloride varied. Curve VII is theoretical.

The value of 13.995 (10) was used for K_W , the ionization constant of water. The concentrations in the ratio in equation 7 were evaluated with the aid of the equations

$$c_{\text{R}^{+-}} = c_{\text{T}} - c_{\text{B}} + c_{\text{OH}^-} \quad (9)$$

$$c_{\text{R}^-} = c_{\text{B}} - c_{\text{OH}^-}$$

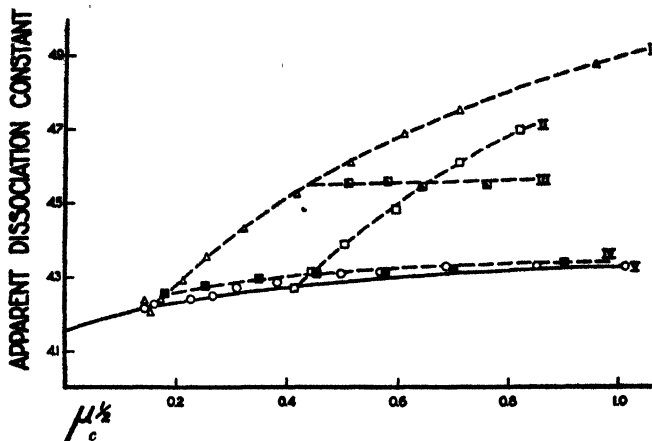


FIG. 5. The effects of sodium chloride, magnesium chloride, and their mixtures on the ionization of alanine in basic solutions. Concentration of alanine, 0.03 *M*. Concentration of sodium hydroxide, 0.021 *M*. Δ = concentration of magnesium chloride varied; \square = 0.15 *M* sodium chloride, concentration of magnesium chloride varied; \blacksquare = 0.08 *M* magnesium chloride, concentration of sodium chloride varied; \blacksquare = 0.00386 *M* magnesium chloride, concentration of sodium chloride varied; \circ = concentration of sodium chloride varied. Curve V is theoretical.

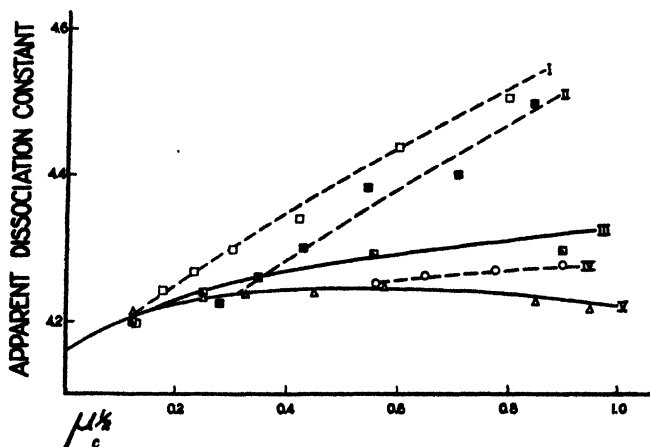


FIG. 6. The effects of potassium chloride, sodium chloride, calcium chloride, and their mixtures on the ionization of alanine in basic solutions. Concentration of alanine, 0.03 *M*. Concentration of sodium hydroxide, 0.015 *M*. \square = concentration of calcium chloride varied; \blacksquare = 0.0625 *M* potassium chloride, concentration of calcium chloride varied; \blacksquare = concentration of sodium chloride varied; \circ = 0.3 *M* potassium chloride, concentration of sodium chloride varied; Δ = concentration of potassium chloride varied. Curves III and V are theoretical.

in which c_B represents the added concentration of sodium hydroxide and c_{OH^-} represents the hydroxyl-ion concentration. The approximation that

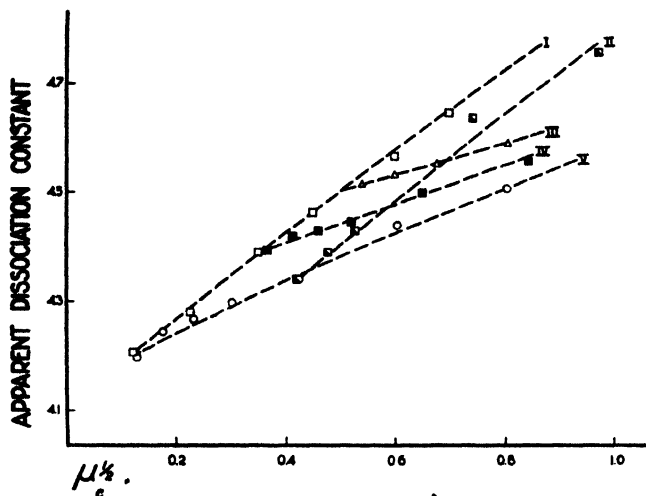


FIG. 7. The effects of calcium chloride, magnesium chloride, and their mixtures on the ionization of alanine in basic solutions. Concentration of alanine, 0.03 *M*. Concentration of sodium hydroxide, 0.015 *M*. □ = concentration of magnesium chloride varied; ■ = 0.0538 *M* calcium chloride, concentration of magnesium chloride varied; △ = 0.0931 *M* magnesium chloride, concentration of calcium chloride varied; ■ = 0.04 *M* magnesium chloride, concentration of calcium chloride varied; ○ = concentration of calcium chloride varied.

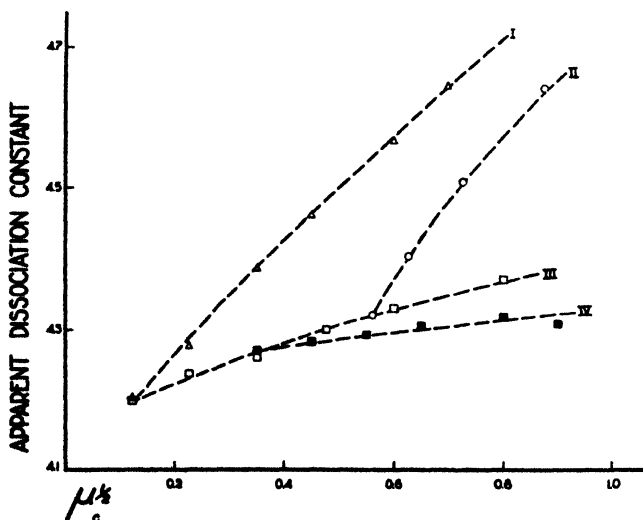


FIG. 8. The effects of barium chloride, sodium chloride, magnesium chloride, and their mixtures on the ionization of alanine in basic solutions. Concentration of alanine, 0.03 *M*. Concentration of sodium hydroxide, 0.015 *M*. △ = concentration of magnesium chloride varied; ○ = 0.01 *M* barium chloride, concentration of magnesium chloride varied; □ = concentration of barium chloride varied; ■ = 0.0358 *M* barium chloride, concentration of sodium chloride varied.

$\alpha_{\text{OH}^-} = \alpha_{\text{OH}^-}$ was employed. Because of the low hydroxyl-ion concentration, any uncertainty resulting from this approximation is considerably less than in the case of the hydrogen-ion concentration appearing in equation 3. The activity of water has been taken as equal to unity in all of the solutions.

The broken lines in the figures have been drawn to fit the experimental points. The solid lines have been calculated according to the theoretical equation

$$-\log K'_B = -\log K_B - \log \gamma_{\text{R}^-} + \log \gamma_{\text{R}^{+-}} + B\mu_c \quad (10)$$

in which K_B is defined by

$$K_B = \frac{\alpha_{\text{R}^{+-}} \alpha_{\text{OH}^-}}{\alpha_{\text{R}^-}} \quad (11)$$

$\log \gamma_{\text{R}^{+-}}$ and $\log \gamma_{\text{R}^-}$ in equation 10 were calculated with the aid of the Debye-Hückel and Kirkwood equations, respectively. The values that

TABLE 2
Values of a' , a , $-\log K_B$, and B

	FIGURE 6 CURVE VII	FIGURE 7 CURVE V	FIGURE 8 CURVE III	FIGURE 9 CURVE V
a' (Debye-Hückel), in Å.	5.0	5.0	5.0	4.65
a (Kirkwood), in Å.	4.3	4.3	4.3	4.6
$-\log K_B$	4.135	4.160	4.160	4.160
B	0.0963	0.0951	0.0951	0.00

were used for the various dimensions that occur in these equations are given in table 2. The values of 3.08 Å. and 4.19 Å., respectively, have been used for b and R in the Kirkwood equation.

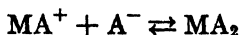
The term $B\mu_c$ may be likened to the "salting-out" term which has been used by Cohn and coworkers (6) to describe the solubilities of amino acids and proteins in salt solutions. The value of B was empirically calculated from the experimental data.

DISCUSSION

The similarity of the effects of the various salts and the theoretical calculations, for the case of the ionization of alanine in acidic solutions, indicates that forces of the type considered in the Debye-Hückel and Kirkwood equations are the chief factors that determine the effects of all of the salts up to moderate salt concentrations. In the case of the ionization in basic solutions, the wide divergence of the effects of the divalent salts from the effects of the monovalent salts and from the theoretical

calculations indicates specific effects of the salts of the alkaline-earth metals.

A possible explanation of the specific effects of the divalent cations is through equilibria of the types



where M^{++} represents Ca^{++} , Ba^{++} , or Mg^{++} and A^{-} represents the alanine anion. It is possible to explain the effects of divalent inorganic cations on the ionization of certain organic acids in terms of mass action constants that apply to equilibria of these types (2). It is not necessary to make a commitment as to the exact nature of the physical forces involved or as to the exact physical natures of the complexes MA^{+} and MA_2 . A second possible explanation, at least in the case of the effects of magnesium chloride, is the formation of the insoluble hydroxide of the metal. The effect of such a precipitation is a decrease in pH and a corresponding increase in $-\log K'_B$. The solutions that were employed for the experiments presented in figure 4 were water-clear. The solutions for the experiments in figure 5 contained a visible precipitate of magnesium hydroxide. Because of the low solubility of magnesium hydroxide, it is not possible to explain the specific effects of magnesium that are apparent in figure 4 on the basis of hydroxide formation. The most probable explanation is, therefore, one that is based on the formation of complexes of the types MgA^{+} , CaA^{+} , BaA^{+} , MgA_2 , CaA_2 , and BaA_2 .

At any one value of the ionic strength in figures 4 and 5, the displacement of the apparent constant by magnesium chloride is greater in figure 5. This, at least in part, may be attributed to the formation of the insoluble hydroxide in the solutions that were employed for the experiments in figure 5.

The difference between curves IV and V or between curves IV and VI in figure 4 is less at high salt concentrations than at low salt concentrations. Simms (17) has noted a similar effect of salt mixtures on the ionization of oxalic acid. Greenwald (7) offered an explanation of these observations of Simms, which is based on the hypothesis of the formation of undissociated complexes between the magnesium ion and the oxalic anion and the effects of changes in the ionic strength, through addition of sodium chloride, on this equilibrium. Because of the similarity of the present results to those of Simms (17), it is considered that the explanation proposed by Greenwald is sufficient for the present case.

No attempt has been made to calculate the theoretical curves for the effects of the divalent cations and the salt mixtures that have been determined in alkaline solutions. Because of the formation of the hydroxides,

the systems are too complex to yield readily to quantitative theoretical treatment.

The data contained in this paper are based on electromotive force measurements of cells that involve a liquid junction. The present work has in a large part been repeated and extended by use of cells that did not involve liquid junctions and therefore the calculations do not involve any extra-thermodynamic assumptions. These data will be reported elsewhere. In general they fit in with the ideas expressed in this paper.

The complete data are on file in the University of California Library.

SUMMARY

1. Certain experiments of Simms concerning the effects of salt mixtures on the pH of alkaline glycine solutions have been repeated. His results have not been verified.

2. The effects of salt mixtures on the ionization of alanine in both alkaline and acidic solutions have been determined.

3. The results have been compared with theoretical calculations, and certain factors that are not accounted for by the theoretical equations have been discussed.

REFERENCES

- (1) BIRGE, R. T.: *Phys. Rev. Suppl.* **1**, 1 (1929).
- (2) CANNAN, R. K., AND KIBRICK, A.: *J. Am. Chem. Soc.* **60**, 2314 (1938).
- (3) CLARK, W. M.: *The Determination of Hydrogen Ions*, 3rd edition. The Williams & Wilkins Co., Baltimore (1928).
- (4) DEBYE, P., AND HÜCKEL, E.: *Physik. Z.* **24**, 185, 305 (1923).
- (5) DEEDS, F.: *Science* **78**, 556 (1933).
- (6) EDSALL, J. T.: In C. L. A. Schmidt's *The Chemistry of the Amino Acids and Proteins*, p. 871. Charles C. Thomas, Springfield (Illinois) and Baltimore (1938).
- (7) GREENWALD, I.: *J. Gen. Physiol.* **22**, 385 (1939).
- (8) KAWAI, S.: *J. Biochem. (Japan)* **6**, 101 (1926).
- (9) KIRKWOOD, J. G.: *J. Chem. Phys.* **2**, 351 (1934).
- (10) LEWIS, G. N., AND RANDALL, M.: *Thermodynamics and the Free Energy of Chemical Substances*. McGraw-Hill Book Company, New York (1923).
- (11) MACINNES, D. A., AND BELCHER, D.: *J. Am. Chem. Soc.* **53**, 3315 (1931).
- (12) MORTON, C.: *J. Chem. Soc.* **1928**, 1401.
- (13) NEUBERGER, A.: *Biochem. J.* **30**, 2085 (1936).
- (14) NEUBERGER, A.: *Proc. Roy. Soc. (London)* **A158**, 68 (1937).
- (15) RUBINSTEIN, D. L.: *Protoplasma* **4**, 259 (1928).
- (16) SCHMIDT, C. L. A., AND HOAGLAND, D. R.: *Univ. California Pub. Physiol.* **5**, 23 (1919).
- (17) SIMMS, H. S.: *J. Gen. Physiol.* **12**, 241 (1928).
- (18) SIMMS, H. S.: *J. Gen. Physiol.* **12**, 783 (1928).
- (19) SPØRSENSEN, S. P. L.: *Compt. rend. trav. lab. Carlsberg* **12**, 1 (1915-17).

THE COMBINATION OF GELATIN WITH ACIDS AND BASES^{1,2}

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The literature on the acid- and base-binding capacity of gelatin contains many values reported by different investigators. Most of these values have been obtained by a study of the combination of gelatin with hydrochloric acid and sodium hydroxide, and they have been accepted by many workers as general values applicable to any acid or base. It was, therefore, thought desirable by the authors that a study of the combination of gelatin with other acids and bases be made in order to determine whether one can correctly accept the combining weights of gelatin with hydrochloric acid and with sodium hydroxide as its equivalent weights as a base and an acid, respectively.

Several values for the combining capacity of gelatin with acids and bases as obtained by different investigators have been listed in table 1. It is to be noted that all work was done with sodium hydroxide and hydrochloric acid except in two cases: namely, the value obtained by Hitchcock (11) for the combination of gelatin with sulfuric acid from conductivity studies, and the value obtained by Chapman, Greenberg, and Schmidt (5) for the combination of gelatin with dyes. It should be further mentioned that much of the difference found in the values listed results from differences in methods of calculation.

THE ACID-BINDING CAPACITY OF GELATIN FROM VISCOSITY STUDIES

In 1929, Bacon (2) reported a value of 1090 for the combining weight of gelatin with hydrochloric acid. This was obtained by studying the viscosity of gelatin-hydrochloric acid solutions to determine the weight ratio of acid to gelatin at the maximum viscosity. The value is in excellent agreement with those obtained by electrometric methods. Bacon used three different concentrations of gelatin with the same result in each case.

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TABLE 1
Acid- and base-binding capacity of gelatin

EQUIVALENTS $\times 10^3$ PER GRAM OF GELATIN	COMBINING WEIGHT	METHOD	DATE	INVESTIGATOR
Acid-binding capacity				
150	665	Electrometric titration	1913	Manabe and Matula (16)
180	770	Electrometric titration	1916	Procter and Wilson (18)
70	1430	Indicator titration	1919	Bracewell (4)
119	840	pH from catalysis	1921	Wintgen and Krüger (21)
300	333	Electrometric titration	1922	Lloyd and Mays (15)
113	885	Electrometric titration	1922	Wintgen and Vogel (22)
92	1090	Electrometric titration	1922	Hitchcock (9)
89	1120	Electrometric titration	1923	Hitchcock (10)
86	1160	Conductivity	1923	Hitchcock (11)
86	1160	Conductivity (H_2SO_4)		
84	1180	Electrometric titration	1924	Atkin and Douglas (1)
104	960	Combination with dyes	1927	Chapman, Greenberg, and Schmidt (5)
92	1090	Diffusion potential	1927	Ferguson and Bacon (7)
93.5	1070	Electrometric titration	1929	Hitchcock (12)
94	1060	Conductivity		
92	1090	Viscosity	1929	Bacon (2)
68	1470	Electrometric titration	1931	Prideaux (17)
300	332	Adsorption of dry hydrogen chloride by dry gelatin	1931	Belden (3)
96	1040	Electrometric titration	1931	Hitchcock (13)
96	1040	Electrometric titration	1932	Hitchcock (14)
Base-binding capacity				
130	770	Electrometric titration	1916	Procter and Wilson (18)
57	1750	Electrometric titration	1925	Cohn (6)
61	1640	Electrometric titration	1931	Prideaux (17)
90	1110	Electrometric titration	1931	Hitchcock (13)
73	1370	Electrometric titration	1932	Ferguson and Schluchter (8)

TABLE 2
Acid-binding capacity of gelatin from viscosity studies

ACID	MAXIMUM RELATIVE VISCOSITY	WEIGHT RATIO ACID TO GELATIN AT MAXIMUM VISCOSITY	ACID-BINDING CAPACITY	
			Equivalents $\times 10^3$ per gram of gelatin	Combining weight
HCl.....	3.25	0.0360	99	1010
HClO ₄	3.13	0.1010	100.5	995
H ₂ SO ₄	2.25	0.0530	108	926
H ₃ PO ₄	3.25	0.1400	143	700
HC ₂ H ₃ O ₂	3.19	4.588	7700	13

It was reasoned that the viscosity change was largely an electroviscous effect and, therefore, the maximum viscosity should coincide with the maximum salt formation or the maximum amount of acid bound.

Since, in the case of gelatin treated with hydrochloric acid, the viscosity maximum yields a value for the combining weight of gelatin which is in good agreement with those obtained by electrometric methods, similar viscosity studies of the combination of gelatin with perchloric, sulfuric, phosphoric, and acetic acids, as well as with hydrochloric acid, have been carried out.

Solutions were made up to contain 0.6000 g. of air-dry (0.5241 g. of bone-dry) Eastman electrodialyzed gelatin and varying amounts of the acids per 100 ml. The viscosities of these solutions were determined at 40°C., using an Ostwald type viscometer. In each case the combining capacity for the particular acid has been calculated from the viscosity maximum. The results are given in table 2.

TABLE 3
Base-binding capacity of gelatin from viscosity studies

BASE	MAXIMUM RELATIVE VISCOSITY	WEIGHT RATIO ACID TO GELATIN AT MAXIMUM VISCOSITY	BASE-BINDING CAPACITY	
			Equivalents × 10 ³ per gram of gelatin	Combining weight
NaOH.....	2.89	0.0500	125	800
KOH	4.26*	0.0520	93	1080
NH ₄ OH.....	2.77†	0.1621	453	216

* 0.987 g. of gelatin per 100 ml.

† 0.473 g. of gelatin per 100 ml.

It is to be observed that the value obtained for the combination of gelatin with hydrochloric acid is in fair agreement with those determined electrometrically, but the values obtained for the other acids show definitely that this combining capacity is specific for hydrochloric acid. Although the values obtained with the other strong acids are quite close to that for hydrochloric, those obtained for phosphoric and acetic acids are so far different that the mechanism in these cases must be different from the mere binding of the hydrogen ion, as has been assumed to be the case for hydrochloric acid.

THE BASE-BINDING CAPACITY OF GELATIN FROM VISCOSITY STUDIES

Viscosity studies, similar to those carried out with the acids, have been made on gelatin solutions containing sodium, potassium, and ammonium hydroxides. The results are given in table 3. Although the value obtained for the combination of gelatin with sodium hydroxide is not in good

agreement with the values listed in table 1, if the weight ratio at maximum viscosity is any measure of the base-binding capacity of gelatin it is quite evident that gelatin binds distinctly different amounts of the three bases studied. As was the case with the acids studied, much larger amounts of the weak base were bound.

**THE ACID-BINDING CAPACITY OF GELATIN FROM ELECTROMETRIC
TITRATION STUDIES**

As a further check on the possible variance of the acid-binding capacity of gelatin for different acids, electrometric titrations have been run on solutions of gelatin with hydrochloric, perchloric, sulfuric, and phosphoric acids. A glass electrode, calibrated against standard phthalate buffer solutions, was used to determine the pH values of the solutions. In each

TABLE 4
Acid-binding capacity of gelatin from electrometric studies

ACID	EXPERIMENT NO.	EQUIVALENTS × 10 ⁴ PER GRAM OF GELATIN	COMBINING WEIGHT
HCl.	1	90	1110
	2	94	1060
			(av. = 1085)
HClO ₄		104	960
H ₂ SO ₄	1	96	1040
	2	95	1050
	3	100	1000
			(av. = 1030)
H ₃ PO ₄		137	730

case the pH was carried to values between 1.5 and 2. All determinations were made at 35°C., and the solutions were weighed at the time of measurement so that correction could be made for changes in concentration due to evaporation of water. Eastman electrodyalized gelatin was used in all the experiments. The concentration of gelatin was kept at approximately 5 per cent in order to minimize the error at low pH values. Calculations of acid bound were made following the procedure outlined by Hitchcock (14).

Table 4 gives the results obtained in these experiments. Activity coefficients used in making the calculations were obtained as follows: for hydrochloric acid, from the data of Scatchard (20); for perchloric acid, the same values used for hydrochloric acid; for sulfuric acid, values from Randall and Scott (19); for phosphoric acid, values obtained by the authors by determining the pH of phosphoric acid solutions with the same apparatus used in the gelatin work.

A comparison of the combining weight values given in tables 2 and 4 shows about as good an agreement as can be expected between such different methods of determination. It is, however, evident that the combination of gelatin with acids and bases is not simply a combination of the gelatin with the hydrogen or hydroxyl ions. Until more is known concerning the effect of gelatin upon the activity coefficients of the hydrogen and hydroxyl ions, the possible hydrolysis of the gelatin in strongly acid and alkaline solution, and about the changes in aggregation produced by high and low pH values, it does not seem possible to interpret these results further.

REFERENCES

- (1) ATKIN AND DOUGLAS: *J. Am. Leather Chem. Assoc.* **19**, 528 (1924).
- (2) BACON: *J. Phys. Chem.* **33**, 1843 (1929).
- (3) BELDEN: *J. Phys. Chem.* **35**, 2164 (1931).
- (4) BRACEWELL: *J. Am. Chem. Soc.* **41**, 1511 (1919).
- (5) CHAPMAN, GREENBERG, AND SCHMIDT: *J. Biol. Chem.* **72**, 707 (1927).
- (6) COHN: *Physiol. Rev.* **5**, 349 (1925).
- (7) FERGUSON AND BACON: *J. Am. Chem. Soc.* **49**, 1921 (1927).
- (8) FERGUSON AND SCHLUCHTER: *J. Gen. Physiol.* **15**, 463 (1932).
- (9) HITCHCOCK: *J. Gen. Physiol.* **4**, 733 (1922).
- (10) HITCHCOCK: *J. Gen. Physiol.* **6**, 95 (1923).
- (11) HITCHCOCK: *J. Gen. Physiol.* **6**, 201 (1923).
- (12) HITCHCOCK: *J. Gen. Physiol.* **12**, 495 (1929).
- (13) HITCHCOCK: *J. Gen. Physiol.* **15**, 125 (1931).
- (14) HITCHCOCK: *J. Gen. Physiol.* **16**, 357 (1932).
- (15) LLOYD AND MAYS: *Proc. Roy. Soc. (London)* **B93**, 69 (1922).
- (16) MANABE AND MATULA: *Biochem. Z.* **52**, 369 (1913).
- (17) PRIDEAUX: *Proc. Roy. Soc. (London)* **B108**, 224 (1931).
- (18) PROCTER AND WILSON: *Trans. Chem. Soc.* **109**, 307 (1916).
- (19) RANDALL AND SCOTT: *J. Am. Chem. Soc.* **49**, 647 (1927).
- (20) SCATCHARD: *J. Am. Chem. Soc.* **47**, 696 (1925).
- (21) WINTGEN AND KRÜGER: *Kolloid-Z.* **23**, 81 (1921).
- (22) WINTGEN AND VOGEL: *Kolloid-Z.* **30**, 45 (1922).

THE RELATION OF CALCIUM PROTEINATE AND COLLOIDAL CALCIUM PHOSPHATE TO THE PARTITION OF CALCIUM IN THE BLOOD STREAM^{1, 2}

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INTRODUCTION

A large amount of effort has been devoted to the problem of determining the factors which control the partition of the blood calcium. Encouraging progress has been made, but a complete solution is not at hand. The complexity of the problem can be seen from the large number of factors which are known to influence the serum calcium partition. These include (a) the concentration and nature of the serum protein, (b) the inorganic phosphate concentration, (c) the magnesium concentration, (d) the pH of the blood, (e) the ionic strength of the serum, and (f) the presence of complex ion forming agents such as citrate, ascorbate, etc. As yet it is not possible to evaluate adequately the effect of many of the above variables.

An important advance in the understanding of the influence of the protein on the partition of the serum calcium has been made through the work of McLean, Hastings, and their associates (16, 17, 18, 24). These workers concluded that the calcium proteinate of the blood serum behaves as a weak electrolyte whose dissociation, as a first approximation, may be described by the mass law equation

$$\frac{[\text{Ca}^{++}] \times [\text{Pr}^{-}]}{[\text{CaPr}]} = K_{\text{CaPr}} \quad (1)$$

This hypothesis was foreshadowed by the observation of Greenberg and Gunther (6) that the protein-bound calcium and diffusible calcium are correlated by means of the Langmuir adsorption isotherm. The mathematical similarity between the Langmuir isotherm and the mass law equation, under certain conditions, has been pointed out by Hitchcock (9).

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² This article is an abstract of a thesis submitted to the Graduate Division of the University of California by Clarence E. Larson in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1937.

In their work, McLean and Hastings employed an ingenious biological method of estimating calcium-ion concentrations in biological fluids, namely, that of determining the response of the frog heart to variations in calcium-ion concentration (17). This technic leads to the conclusion that virtually all of the diffusible calcium of normal blood serum is in an ionized condition. The shortcoming of this method is that the frog heart is quite limited with respect to the concentration range over which it is sensitive, the upper limit being about 2.0 millimoles of Ca^{++} .

As has been pointed out by McLean (15), a number of uncertain assumptions are involved in the numerical treatment by McLean, Hastings, and their associates of the calcium proteinate dissociation equation. The most important is the use of the hydroxide titration value of a protein as a measure of the calcium-combining groups of the protein; or, in other words, that it represents the molal concentration of the protein with respect to its calcium-combining group. A second assumption is that the serum protein behaves toward calcium as if it were a series of divalent ions. The present investigation is devoted to a study of the influence of the serum protein and colloidal calcium phosphate on the partition of the serum calcium, employing quite different experimental and mathematical procedures in an effort to eliminate the experimental shortcomings and the assumptions of doubtful accuracy pointed out above. The partition of the calcium and inorganic phosphate was determined by ultrafiltering the blood serum through collodion membranes. Ultrafiltration was carried out by a modification of the method of Greenberg and Gunther (6).³ The range of concentrations of the calcium and protein fractions were extended experimentally by (a) injections of calcium salts, (b) production of hypervitaminosis D, and (c) parathormone injections. Alterations *in vitro* were produced by merely adding calcium chloride in amounts necessary to produce the desired level. So far as may be judged, the variations between *in vivo* experiments and *in vitro* experiments are no greater than the variations within each group. Alteration in protein was produced by plasmapheresis.

MATHEMATICAL TREATMENT OF THE DATA

Chemical symbols without brackets have been used to represent concentrations in milligrams per 100 ml. of serum, except for proteins which are given in grams per 100 ml. Bracketed symbols will designate concentrations in moles per liter. The symbols TPr, TCa, etc., will be used for total protein, total calcium, etc. Pr^{--} will represent protein ion, CaPr calcium proteinate, and Ca_D^{++} diffusible calcium.⁴

³ Full details of the experimental and analytical procedures are given in the thesis of C. E. Larson (11).

⁴ For the evidence that the diffusible calcium is virtually all ionized, see references 3 and 16.

The mathematical treatment of the partition of serum calcium in this work, as in that of McLean and Hastings, is based upon the assumption that the dissociation of the calcium proteinate is governed by the law of mass action. The mass law equation can be represented most simply when all of the variables concerned can be expressed in units of molar concentration. In that event one can write:

$$\frac{[\text{Ca}^{++}] \times [\text{Pr}^{--}]}{[\text{CaPr}]} = K_{\text{CaPr}} \quad (2)$$

since

$$[\text{TPr}] = [\text{CaPr}] + [\text{Pr}^{--}] \quad (3)$$

On substituting for $[\text{Pr}^{--}]$ there is obtained

$$\frac{[\text{Ca}^{++}] \times ([\text{TPr}] - [\text{CaPr}])}{[\text{CaPr}]} = K_{\text{CaPr}} \quad (4)$$

Rearranging gives

$$\frac{[\text{TPr}]}{[\text{CaPr}]} = 1 + \frac{K_{\text{CaPr}}}{[\text{Ca}^{++}]} \quad (5)$$

Equation 5 shows that a plot of $[\text{TPr}]/[\text{CaPr}]$ against $1/[\text{Ca}^{++}]$ should yield a straight line in which the slope will be equal to K_{CaPr} , and the intersection on the $[\text{TPr}]/[\text{CaPr}]$ axis will be 1.

Since the results of the serum calcium partition are not commonly expressed in units of molar concentrations, it is desirable to show the relationship which exists between the molar units and the more commonly employed method of representing calcium values in milligrams per 100 ml. and protein in grams per 100 ml. of serum.

In the latter case, the mass law equation may be written as:

$$\frac{\text{Ca}_D^{++} \times \text{Pr}^{--}}{\text{CaPr}} = B \text{ (a constant)} \quad (6)$$

The protein-ion concentration is obtained from the relation:

$$\text{Pr}^{--} = \text{TPr} - \frac{\text{CaPr}}{A} \quad (7)$$

where A is a conversion factor which represents the calcium-combining power of the protein expressed in milligrams of calcium per gram of protein. Substituting in equation 7 for Pr^{--} there is obtained:

$$\frac{\text{Ca}_D^{++} \times \left(\text{TPr} - \frac{\text{CaPr}}{A} \right)}{\text{CaPr}} = B \quad (8)$$

From this

$$\frac{\text{TPr}}{\text{CaPr}} = \frac{1}{A} + \frac{B}{\text{Ca}_D^{++}} \quad (9)$$

According to this equation, if TPr/CaPr is plotted against $1/\text{Ca}_D^{++}$, a straight line is obtained, the slope of which is equal to B , and the intersection on the TPr/CaPr axis is equal to $1/A$. The relationship between the constants $1/A$ and B of equation 9 and K_{CaPr} of equation 5 may be seen from the following considerations.

The relations between concentrations in moles and the commonly employed weight units may be represented by

$$\begin{aligned} 4[\text{Ca}^{++}] \times 10^3 &= \text{Ca}_D^{++}; \quad 4[\text{CaPr}] \times 10^3 = \text{CaPr}; \\ \frac{4[\text{Pr}^{--}]}{A} \times 10^3 &= \text{Pr}^{--} \end{aligned} \quad (10)$$

On substituting the corresponding values in equation 6 there is obtained

$$\frac{4[\text{Ca}^{++}] \times 10^3 \times 4[\text{Pr}^{--}] \times 10^3}{4[\text{CaPr}] \times 10^3 A} = B \quad (11)$$

or

$$\frac{[\text{Ca}^{++}] \times [\text{Pr}^{--}]}{[\text{CaPr}]} = \frac{BA}{4 \times 10^3} \quad (12)$$

which is identical with equation 2. Therefore,

$$K_{\text{CaPr}} = \frac{BA}{4 \times 10^3} \quad (13)$$

This derivation shows that the calcium protein dissociation constant in molar units is given by the product of the constants $B \times A$ over 4×10^3 when the concentration of calcium is expressed in milligrams per cent and serum protein in grams per cent.

EXPERIMENTAL RESULTS

Colloidal calcium phosphate

Before the relationship between calcium and protein can be examined in the present experiments, the effect of the formation under certain special conditions of a non-diffusible colloidal complex of calcium and phosphate in the blood must be considered. Under normal physiological conditions in man and apparently in most animals, the inorganic phosphate of the serum is completely diffusible. In the fowl a considerable fraction of the inorganic phosphate is normally in a non-diffusible condition (5, 12). When the product of the calcium-ion and phosphate-ion concentrations is

increased, the solution stability of some calcium phosphate compound is apparently exceeded and it appears in the blood stream in a colloidal form. The literature concerning this phenomenon has been reviewed by Schmidt and Greenberg (21) and by Greenberg (2).

Evidence for the presence of colloidal calcium phosphate is found in conditions in which there is a hypercalcemia. Experimentally, this may

TABLE 1
*Formation of colloidal calcium phosphate in blood serum**

TIME	SERUM Ca	DIFFUSIBLE Ca	NON- DIFFUSIBLE Ca	INORGANIC P	NON- DIFFUSIBLE P	COLLOIDAL Ca ₃ (PO ₄) ₂	CALCIUM PROTEIN- ATE
A. Human blood serum augmented with calcium							
	2.76	1.57	1.19	1.35	0.03	0.015	1.14
	4.20	2.24	1.96	1.35	0.29	0.15	1.54
	5.20	3.10	2.19	1.29	0.29	0.15	1.75
	6.40	3.32	3.08	1.29	0.55	0.28	2.27
	7.55	3.58	3.98	1.29	0.90	0.45	2.63
	8.68	4.47	3.94	1.26	0.58	0.29	3.05
	9.93	5.55	4.38	1.26	0.93	0.46	3.00
B. Following intravenous injection of calcium gluconate (dog G—0.5 g. Ca)							
0	2.80	1.80	1.00	1.70			1.00
0.1 hr.	5.20	3.60	1.60	1.40	0.35	0.17	1.08
0.33 hr.	5.65	3.65	2.00	1.35	0.45	0.22	1.33
C. Following injection of parathyroid hormone (dog G—500 units)							
0	3.05	1.60	1.45	2.77	0.24	0.12	1.08
6.5 hr.	3.83	1.83	2.00	1.80	0.32	0.16	1.52
28 hr.	4.65	2.73	1.92	2.22	0.30	0.15	1.77
D. Following administration of viosterol (dog J—500,000 units)							
0	2.70	1.46	1.24	1.43			1.24
39 days	3.17	1.67	1.50	2.05	0.17	0.08	1.25
46 days	4.30	2.10	2.20	2.00	0.47	0.24	1.50
48 days	4.00	2.12	1.88	1.71	0.37	0.18	1.38

* Analytical values are expressed in millimoles per liter of serum.

be produced by injection of calcium salts, of massive doses of parathyroid extract, or of irradiated ergosterol. Colloidal calcium phosphate is also formed in conditions with hyperphosphatemia, but here a much greater increase in the product of the calcium-ion and phosphate-ion concentrations is necessary. This indicates that the formation of the colloid is not a simple supersaturation phenomenon.

Experiments which illustrate the formation of the colloidal calcium phosphate are given in table 1.

At present there is no direct way to determine the composition of the colloidal calcium phosphate. An indirect method of arriving at the formula seems available from a combination of the conditions required by the calcium partition of the blood serum and the mass law dissociation of the calcium proteinate.

When the blood contains colloidal calcium phosphate, the non-diffusible calcium consists of calcium proteinate and calcium as colloidal phosphate. The calcium in the latter form is directly proportional to the non-diffusible inorganic phosphorus of the serum, the proportionality factor being dependent upon the chemical constitution of the colloidal phosphate.

If the calcium proteinate is calculated as the difference between non-diffusible calcium and colloidal phosphate calcium, assuming the formulas probable for the composition of this substance, the one which yields values of calcium proteinate that give a straight line when TPr/CaPr is plotted against $1/\text{Ca}_D^{++}$ furnishes the probable composition of the colloidal calcium phosphate. Treatment of the experimental data of the present work in this manner yielded the formula $\text{Ca}_3(\text{PO}_4)_2$ for the composition of the colloidal calcium phosphate. This is illustrated in table 1.

Dissociation of calcium proteinate

By *in vivo* and *in vitro* augmentation of the calcium of the blood serum, data were obtained from a large number of experiments which, after correcting for the presence of colloidal calcium phosphate, could be treated statistically to determine the correlation between calcium and protein. A plot of TPr/CaPr against $1/\text{Ca}_D^{++}$ seemed to indicate that the best fit of the points was obtained by a straight line, as would be expected from the relationships given by equations 5 and 9. This is shown in figure 1. A statistical evaluation of the correlation between these variables yielded the highly significant result: $r_{1,2} = 0.728 \pm 0.034$.

From the statistical treatment of the experimental data, the following numerical representations of equations 5 and 9 were obtained:

$$\frac{\text{TPr}}{\text{CaPr}} = 0.4035 + \frac{5.80}{\text{Ca}_D^{++}} \quad (14)$$

when the concentrations are expressed in milligrams of calcium and grams of protein per 100 ml. of serum. When the variables are expressed in concentrations of moles per liter, the equation becomes

$$\frac{[\text{Pr}]}{[\text{CaPr}]} = 1 + \frac{3.60 \times 10^{-3}}{[\text{Ca}_D^{++}]} \quad (15)$$

In equation 14, derived from the data plotted in figure 1, the value 0.4035 is the constant $1/A$ of equation 10. From this it follows that the

maximum calcium-combining power per gram of serum protein is 2.48 mg. or 0.062 millimole. By the method of treatment employed in this work, the conversion factor for reducing grams of protein to millimoles of protein has been directly determined from the results obtained from experiments performed under conditions which approximate the natural state of the proteins and calcium in the animal body. Equation 15 shows that the dissociation constant of the calcium proteinate, $K_{CaPr} = 3.60 \times 10^{-3}$, or $pK_{CaPr}^5 = 2.44$.

McLean and Hastings and their associates assumed that the calcium-combining value of the serum protein was equivalent to its alkali-combining

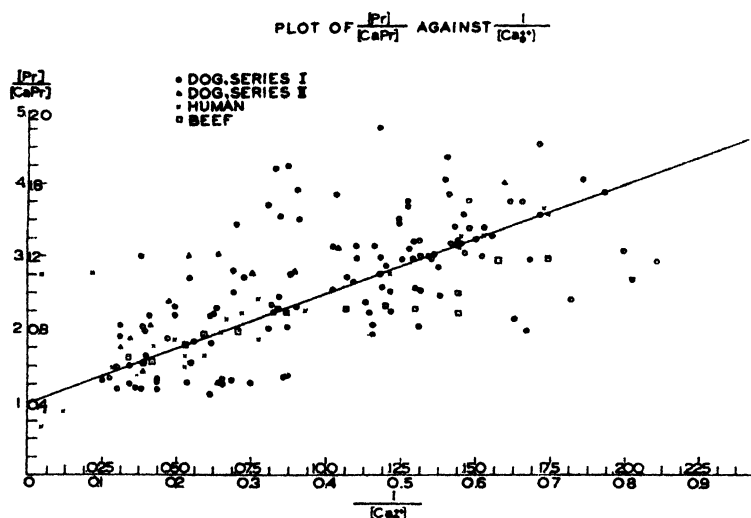


FIG. 1. The method of plotting the calcium partition data of blood sera augmented with calcium in order to determine the calcium-combining capacity of the serum protein and the dissociation constant of the calcium protein compound. The outer scales represent concentrations in millimoles per liter and the inner scales milligrams per 100 ml. of serum.

capacity and used the conversion factor derived from the titration curves of the serum proteins carried out by Van Slyke, Hastings, Hiller, and Sendroy (23). From the titration values at pH 7.35 they obtained 0.1215 as the conversion factor from grams to millimoles of protein. Since 0.1215 is approximately twice the calcium conversion factor of 0.0622, obtained by us, the inference exists that only half as many calcium ions as OH^- ions are capable of uniting with the protein at this pH. Using the conversion factor from the titration data, McLean and Hastings obtained the value for the dissociation of the calcium proteinate of $pK_{CaPr} = 2.22$. If their

⁵ pK = the negative logarithm of the dissociation constant.

results are recalculated on the basis of the conversion factor obtained in this work, the dissociation constant becomes $pK_{CaPr} = 2.63$.

Because of the discrepancy between the results of the two investigations, it was desirable to check the results with other available data. Such a check (calculation of pK_{CaPr}) can be derived from the summary of the average normal calcium partition compiled by Schmidt and Greenberg. From this compilation (21, pages 332 and 333), there are obtained the values of $pK_{CaPr} = 2.45$ for human blood serum, and $pK_{CaPr} = 2.30$ for dog blood serum.

The constants obtained from the different sources have been tabulated in table 2, for ready comparison.

The magnitude of the dissociation constant for the calcium proteinate of blood serum from the various sources (table 2) agrees only in the order of magnitude of the values. Recent attempts to apply the dissociation equation to the calcium partition in the blood in pathological conditions and to species other than man have met with but qualitative success

TABLE 2
Calcium proteinate dissociation constants

	VALUE OF MC LEAN AND HASTINGS (16)	MC LEAN AND HASTINGS DATA, USING NEW PROTEIN CONVERSION FACTOR	VALUE FROM PRESENT WORK	AVERAGE OF SERUM CALCIUM PARTITION	
				Human serum	Dog serum
K_{CaPr}	6.03×10^{-3}	2.30×10^{-3}	3.60×10^{-3}	3.57×10^{-3}	4.95×10^{-3}
pK_{CaPr}	2.22	2.64	2.44	2.45	2.30

(1, 7, 19, 20). The probable explanation for this is that the nature of the component proteins of the serum, and, as a consequence, the calcium-combining capacity of the serum protein, is more variable than has been assumed in this work. The complex and heterogeneous nature of the protein of the blood serum has been emphasized by recent investigations (8, 10, 22), and the evidence indicates that both albumin and globulin are a mixture of labile proteins.

Relative calcium-combining power of albumin and globulin

The combining relation between calcium and the different protein fractions has been incompletely studied. The previous work has been carried out by isolating the protein fractions (4, 13, 14, 16) in order to study the calcium-combining relations of the individual protein components. This involves the danger that the proteins may become denatured and thus altered in their calcium-combining capacity during the course of their isolation. Plasmapheresis offers a good means of altering not only the total protein content but also the ratio between the albumin

and globulin of the blood serum, from the values in normal serum of between 1.5 to 2.5 parts of albumin to 1 part of globulin. Shifts in the ratio of the serum proteins are found in many pathological conditions and also can be produced by a variety of experimental measures. In the present work an estimate has been made of the total albumin and globulin calcium-combining capacity under conditions as they occur in the animal organism through a statistical analysis of the results of the alterations in the calcium partition produced by the plasmapheresis.

The degree of correlation between calcium proteinate and total protein is of interest as a test of the dependence of the serum calcium upon the protein level, since, if our theories are correct, there should be an increase in the non-diffusible calcium with increasing protein concentration. The

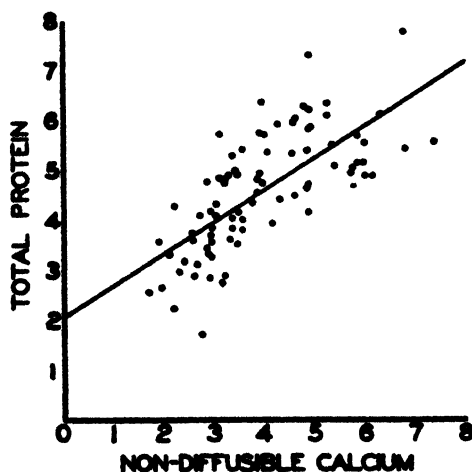


FIG. 2. Correlation diagram of serum protein against non-diffusible calcium from the results of plasmapheresis experiments with dogs.

data from the plasmapheresis experiments yielded the value of $r_{1,2} = 0.710 \pm 0.035$ for the calcium correlation between proteinate and total serum protein. The correlation diagram for the data is plotted in figure 2. The high correlation obtained is valuable supplementary evidence for the theory of the combination of calcium with protein in biological fluids.

Since all experiments up to the present on the relative calcium-combining power of the albumin and globulin fractions of serum have been carried out under conditions which probably involve denaturation, it has been uncertain how much significance can be attached to the results. In order to throw some light on the relative importance of the albumin and globulin to the calcium-combining power of blood serum, correlations were calculated between the non-diffusible calcium and the albumin and globulin content. It has been assumed in the past that the albumin combines with

more calcium per gram and also, since albumin is present in greater quantity, it would naturally be expected that the correlation between albumin and CaPr would be greater than that between globulin and CaPr. The correlations obtained, $r_{1,2} = 0.612 \pm 0.045$ between albumin and CaPr, as against $r_{1,2} = 0.328 \pm 0.063$ between globulin and CaPr, bear out this prediction. As would be expected, the correlation between CaPr and albumin is lower than the correlation between CaPr and total protein, owing to the fact that the globulin also combines with an appreciable amount of calcium. Also, since the globulin is less important than the albumin in combining with the protein, the lower correlation obtained for it is comprehensible.

In an effort to determine the exact calcium-combining capacity of each of the protein fractions, the data from the plasmapheresis experiments were examined to see if a quantitative relationship could be derived. Assuming that, in serum, part of the non-diffusible calcium is bound to the albumin and part to the globulin, the following algebraic expression can be set up:

$$Ax + Gy = \text{CaPr} \quad (16)$$

where A = the albumin concentration in grams per 100 ml., x is the calcium-combining power per gram of albumin, G = the globulin concentration in grams per 100 ml., and y is the calcium-binding power per gram of globulin.

Since A , G , and CaPr can be determined analytically, x and y are the only unknowns. By varying experimentally the ratios of albumin to globulin, we can obtain values to substitute in the simultaneous equations which render them capable of solution.

In the plasmapheresis experiments, by removing the plasma proteins and following their regeneration, there are obtained different ratios of albumin to globulin, and with these data it was possible to evaluate the equations according to the following scheme:

$$A_{\text{low ratio}} + G_{\text{low ratio}} = \text{CaPr}_{\text{low ratio}} \quad (17)$$

$$A_{\text{high ratio}} + G_{\text{high ratio}} = \text{CaPr}_{\text{high ratio}} \quad (18)$$

From eighty-two such ratios there were obtained the numerical equations:

$$122.6x + 53.39y = 153.43; \quad 122.48x + 93.10y = 174.41 \quad (19)$$

The solution yielded the values $x = 0.916$ and $y = 0.772$.

Therefore, from this derivation, it is deduced that 1 g. of albumin can combine with 0.916 mg. or 0.229 millimole of calcium, and that 1 g. of globulin can combine with 0.772 mg. or 0.0193 millimole of calcium at a normal level of diffusible serum calcium. It must be emphasized that

these figures apply only to the normal calcium levels found in blood, and do not represent the maximum calcium-combining capacities of the protein.

The importance of these results lies in the common use of the total serum protein to calculate the ionization of the calcium of the blood serum, without regard to alterations in the ratio of albumin to globulin. The data obtained show that the albumin and globulin calcium-combining capacities are sufficiently close together so that presumably the total protein can ordinarily be used safely to calculate the calcium ionization to a first approximation. However, evidence exists that in certain pathological conditions the serum protein make up may be so altered as to yield extremely erroneous results (7).

SUMMARY

1. A study has been made of the calcium partition of the blood serum by means of ultrafiltration, in which calcium was varied by injection of calcium salts, of parathyroid hormone, and of large doses of vitamin D. Variation in the serum protein has been produced by plasmapheresis.

2. Evidence is offered for the formation of a colloidal form of calcium phosphate in serum when there is an increase in the product of the concentrations of calcium and phosphate ions. The substance is probably a colloidal form of $\text{Ca}_3(\text{PO}_4)_2$.

3. A linear equation based on the law of mass action governing the relations between calcium and total serum protein has been derived. From the application of this equation to the experimental data, the dissociation constant of the calcium proteinate and the maximum calcium-combining power of the protein of the serum have been evaluated.

4. The technic of plasmapheresis has been used to obtain data from which the calcium-combining power of albumin and globulin was derived for normal blood calcium levels.

REFERENCES

- (1) DUCKWORTH, J., AND GODDEN, W.: *Biochem. J.* **30**, 1560 (1936).
- (2) GREENBERG, D. M.: *Ann. Rev. Biochem.* **8**, 269 (1939).
- (3) GREENBERG, D. M., AND GREENBERG, L. D.: *J. Biol. Chem.* **99**, 1 (1932).
- (4) GREENBERG, D. M.: *J. Biol. Chem.* **79**, 177 (1928).
- (5) GREENBERG, D. M., LARSON, C. E., PEARSON, P. B., AND BURMESTER, B. R.: *Poultry Sci.* **15**, 483 (1936).
- (6) GREENBERG, D. M., AND GUNTHER, L.: *J. Biol. Chem.* **85**, 491 (1930).
- (7) GUTMAN, A. B., AND GUTMAN, E. C.: *J. Clin. Investigation* **16**, 903 (1937).
- (8) HEWITT, L. F.: *Biochem. J.* **31**, 360, 1047, 1534 (1937); **32**, 26 (1938).
- (9) HITCHCOCK, D. I.: *J. Am. Chem. Soc.* **48**, 287 (1926).
- (10) KEKWICK, R. A.: *Biochem. J.* **32**, 552 (1938).
- (11) LARSON, C. E.: Thesis, University of California, 1937.
- (12) LASKOWSKI, M.: *Biochem. Z.* **260**, 230 (1933).

- (13) LOMB, R. F., AND NICHOLS, E. G.: J. Biol. Chem. **72**, 687 (1927).
- (14) MARRACK, J., AND THACKER, G.: Biochem. J. **20**, 580 (1926).
- (15) McLEAN, F. C.: Physiol. Rev. **18**, 495 (1938).
- (16) McLEAN, F. C., AND HASTINGS, A. B.: J. Biol. Chem. **108**, 285 (1935).
- (17) McLEAN, F. C., AND HASTINGS, A. B.: J. Biol. Chem. **107**, 337 (1934).
- (18) McLEAN, F. C., AND HASTINGS, A. B.: Am. J. Med. Sci. **189**, 601 (1935).
- (19) MORISON, R. S., McLEAN, R., AND JACKSON, E. B.: J. Biol. Chem. **122**, 430 (1938).
- (20) OBERST, F. W., AND ANDERSCH, M.: J. Clin. Investigation **15**, 131 (1936).
- (21) SCHMIDT, C. L. A., AND GREENBERG, D. M.: Physiol. Rev. **15**, 297 (1936).
- (22) TISELIUS, A.: Biochem. J. **31**, 313, 1464 (1937).
- (23) VAN SLYKE, D. D., HASTINGS, A. B., HILLER, A., AND SENDROY, J., JR.: J. Biol. Chem. **79**, 769 (1928).
- (24) WEIR, E. G., AND HASTINGS, A. B.: J. Biol. Chem. **114**, 297 (1936).

A PRACTICAL MODEL OF THE ANIMAL CELL MEMBRANES¹

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Animal cell walls as living membranes permit the passage of water-soluble or fat-soluble substances to nourish the cell. This perplexing, yet essential, behavior has been explained by a number of theories, but no satisfactory working models have been offered to the biologist.

Osterhout (4) in a condensed statement wrote, "It had been suggested by Quincke that the outer layer of the cell consists of a film of oil: Overton came to a similar conclusion, substituting for 'oil' the term 'lipoid', which includes such substances as lecithin and cholesterin."

Kahlenberg (2) separated water-soluble substances from one another by dialysis through membranes of thin silk saturated with lanolin and through parchment bags impregnated with lanolin. He thought that the selective properties were due to the cholesterol in the lanolin. In his own words, "It would seem likely that sterols give living cells their wonderful selective osmotic properties."

Clowes (1) suggested that living membranes resembled emulsions so near the balance between oil-in-water and water-in-oil types as to be affected differently in respect to permeability by monovalent and divalent cations.

Single permeability is well known with membranes of collodion formed by evaporation of the ether and removal of alcohol by washing with water or with toluene. The first is used in dialysis of water solutions, while the second is useful only in dialysis of toluene solutions (or "oils"), but neither membrane shows the double permeability of living animal cell membranes.

It seemed that if some substance such as lecithin, oleic acid, or rosin could be incorporated in common collodion solution, the resulting membranes might offer continuous, although irregular, paths of two types of material for migration of both water-soluble and fat-soluble substances.

Lecithin dissolved readily in common collodion solution, but a 1 per cent solution was selected from a number of concentrations tried. After allowing the ether component to evaporate and washing out the alcohol

¹ Presented at the Sixteenth Colloid Symposium, held at Stanford University, California, July 6-8, 1939.

with water, the resulting bag (almost transparent) was filled with water containing about 1 per cent sodium chloride and was hung in a vessel of water containing a slight amount of silver nitrate as indicator. In 4 sec. an initial opalescence or cloudiness appeared in the outer solution. The membrane was therefore permeable to water solutions.

Another collodion-*lecithin* bag filled with toluene (to represent lipid solvents) which had been dyed red with Sudan III was hung in a vessel of colorless toluene. In 1.5 min. the red solution appeared in the outer liquid. Evidently the same membrane was permeable to water solutions and to toluene solutions.

A 15 per cent solution of a fat (cottonseed oil) in toluene was dialyzed against pure toluene while samples of the dialysate were frequently withdrawn for fat spot tests on paper. In 15 min. appreciable amounts of fat had gone through the collodion-*lecithin* membrane.

Next, a similar bag containing an emulsion of fat (dyed red) in water, with sodium oleate as emulsifying agent, was hung in a beaker containing a layer of toluene resting on a layer of water. Within 3 sec. some sodium chloride in the water of the emulsion passed through the membrane and formed faint opalescence with a trace of silver nitrate in the outer water layer. At the same time red drops of fat passed through and dissolved in the colorless toluene layer. Incredible as it seems, red drops also formed on the areas of the membrane immersed in water. These drops, seen after 5 sec., often coalesced and rose into the upper toluene layer. Evidently the emulsion film of sodium oleate broke on contact with the collodion-*lecithin* membrane. With gelatin as emulsifying agent no oil passed through.

This emulsion procedure described above was reversed by using a water-in-oil emulsion prepared by dispersing water in a solution of gum dammar in toluene. The water was dyed with fluorescein and the toluene with Sudan III. When a sac filled with this emulsion was hung in toluene, drops of colored water appeared on the outside of the sac.

Other substances were used successfully in place of *lecithin*. Oleic acid, stearic acid, rosin, cholesterol, and a 5:1 mixture of *lecithin* and cholesterol (to simulate their natural occurrence in animal cells) gave collodion membranes double permeability, although there was some variation in the speed of diffusion. As a rule 1 per cent solutions were most satisfactory, although a 1.5 per cent solution of *lecithin* was used to advantage.

It is noteworthy that soaking a collodion-oleic acid membrane in toluene for 18 hr. to replace the oleic acid with toluene decreases the permeability to water considerably, although permeability to toluene remains high.

Pervaporation (3) through an ordinary collodion sac containing 78 g. of water, heated only by summer sunshine, showed a loss of 15 per cent in 2 hr. A membrane prepared from collodion, containing 1 per cent of lecithin, permitted a 9 per cent loss of water. Pervaporation of toluene through a collodion membrane, prepared by washing out the alcohol with toluene, permitted a 35 per cent loss of toluene in 2 hr., while the usual collodion-lecithin membrane permitted a toluene loss of 28 per cent. Variations in intensity of sunshine doubtless caused some error in these results but do not change the fact of remarkable double permeability. Pervaporation can be used as a simple test for membrane quality.

SUMMARY

1. A working model of animal cell membranes of double permeability can be prepared quickly and simply.

2. A membrane permeable to water-soluble and also to fat (or lipid)-soluble substances is made by dissolving lecithin (1 per cent) in common collodion solutions of cellulose nitrate, evaporating the ether as the fluid is swirled in a beaker or flask, and washing out the alcohol with water.

3. The addition to collodion solutions of 1 per cent of oleic acid, stearic acid, cholesterol, a 5:1 mixture of lecithin and cholesterol, rosin, and similar substances also permits formation of good membranes of double permeability.

4. When a collodion-lecithin sac containing an emulsion of toluene (dyed red with Sudan III) in water containing sodium oleate as emulsifying agent is hung in a beaker of water, red drops of toluene form on the outside of the sac.

5. Collodion-lecithin sacs filled with water and hung in warm sunshine lose water rapidly by pervaporation. Similar sacs filled with toluene lose toluene rapidly, showing double permeability.

6. Collodion-lecithin membranes are more slowly permeable to solutions of fats in toluene.

Credit is due W. Alexander, J. Gofman, and D. Adams for laboratory assistance in this research.

REFERENCES

- (1) CLOWES, G. H. A.: *J. Phys. Chem.* **20**, 407 (1916).
- (2) KAHLBERG, L.: *Phil. Mag.* **1**, 385 (1926).
- (3) KOBER, P. A.: *J. Am. Chem. Soc.* **39**, 944 (1917).
- (4) OSTERHOUT, W. J. V.: *Some Fundamental Properties of Cellular Physiology*. Yale University Press, New Haven (1927).

THE USE OF ZEOLITIC MEMBRANE ELECTRODES^{1, 2}

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I. INTRODUCTION

The widespread use of the glass membrane electrode for the comparison of hydrogen-ion activities has caused some attention to be devoted to the determination of other cations. It has been shown that the glass membrane electrode itself responds both to hydrogen and to other cations when the concentration of these is sufficiently high (3). Variations in the composition of the glass are known to be important in this connection (8). However, the detailed properties of glass membranes showing sensitivity to various cations have been but little investigated.

The possibility that insoluble minerals containing calcium might act as selective membranes, thus enabling calcium-ion activities to be compared, was suggested by Tendeloo (9), but his membranes gave much smaller potentials than would be expected theoretically. As was pointed out by Anderson (1), these are probably to be regarded as crack electrodes. The reply of Tendeloo (10), however, still leaves the true status of these electrodes an open question.

The investigations of Michaelis and his pupils on the properties of dried collodion membranes (7, 12) clearly demonstrated that within the membrane the apparent transport of electricity by the anion almost disappeared at low concentrations, so that a comparison of the cationic activities became feasible. All monovalent cations, independently of the anion with which they were combined, behaved in this way. The divalent and trivalent cations, for some as yet unexplained reason, did not give regular potential differences, and apparently only the hydrogen ions present could be measured in such solutions. An important characteristic of these dried collodion membranes was the fact that as the concentration of the monovalent cations increased, the potential difference for a given concentration ratio decreased. This decrease was much larger than that which would be

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anticipated from the ionic activities. It is known as the "concentration effect."

More recently, the question of membrane potentials has been theoretically investigated by Teorell (11) and by Meyer and Sievers (4, 5, 6). In these studies the membrane has been regarded as permeable to anions, cations, and solvent molecules. The charge on the membrane framework is taken into consideration in evaluating two Donnan potentials, one on each surface. In addition there is a liquid junction potential within the membrane. We thus have three possible membrane types, as listed below.

(1) The membrane is uncharged and merely assists the formation of a normal liquid junction by preventing convection. The ordinary liquid junction formula applies, and complicated cases can be calculated by the Henderson or Planck formulae.

(2) The membrane acts in some way as an ionic sieve, preventing either anions or cations from passing through. We are here concerned with the case in which anions are held back. This could conceivably occur by mechanical restriction, since metallic cations are smaller than all anions except OH^- and F^- . The equation for the membrane potential would then be similar to that used for hydrogen with the glass electrode. The glass electrode represents the extreme case of impermeability to all anions except perhaps OH^- , and great restriction on all cations except H^+ .

However, the experimental realization of a membrane exercising complete restraint on all anions, yet permeable to all cations, seems impossible. If the membrane is sufficiently porous so that it can conduct by the movement of various cations, then water molecules are also likely to penetrate it; that is, we shall be dealing with a hydrated membrane. But the presence of water molecules involves the $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$ equilibrium; hence some mobile anions are present within the membrane. But if hydroxide ions within the membrane can transport electricity, then other anions outside may also participate indirectly, by interchange at the surface.

Thus in any hydrated membrane we must expect some conductance due to anion movement, but in favorable cases this may be sufficiently small to be neglected. In alkaline solutions, however, it is likely to be important.

(3) The case considered by Teorell and by Meyer involves only the kind of restraint on ionic movement which the membrane can exert by virtue of its electric charge. Thus it is entirely possible to have this effect superimposed upon the simple sieve action considered under (2), and we shall see that the cationic membranes used here have such an intermediate character. In the equation given by Meyer and Sievers (4, 5, 6) and by Teorell (11) the relative mobilities of the anions and cations within the

membrane are generally assumed to be different from those in the pure solvent and the ratio U_c/U_A for a pair of ions having equal mobilities in water gives a measure of the restrictive or sieve action of the membrane. In the absence of such sieve action the potential difference across the membrane is determined by the following factors: the charge on the membrane expressed as an ionic activity and denoted by A , the relative mobilities of anion (U_A) and cation (U_c) in water, and the concentrations on the two sides of the membrane, C_1 and C_2 .

The equation for the case of a membrane whose charge is balanced by monovalent cations of the same kind as those in the two solutions (the anions of which are also monovalent) is as follows:

$$E = \frac{RT}{F} \cdot \left\{ U \ln \frac{\sqrt{\frac{4C_2^2}{A^2} + 1} + U}{\sqrt{\frac{4C_1^2}{A^2} + 1} + U} + \frac{1}{2} \ln \frac{\left(\sqrt{\frac{4C_1^2}{A^2} + 1} + 1\right)\left(\sqrt{\frac{4C_2^2}{A^2} + 1} - 1\right)}{\left(\sqrt{\frac{4C_1^2}{A^2} + 1} - 1\right)\left(\sqrt{\frac{4C_2^2}{A^2} + 1} + 1\right)} \right\}$$

where

$$U = \frac{U_c - U_A}{U_c + U_A}$$

We now choose a suitable fixed ratio of concentrations such as $C_1:C_2 = 1:10$, so that E becomes simply a function of U and of C_1/A . A family of curves can now be plotted by assigning arbitrary values to U_c/U_A and expressing E as a function of A/C_1 or, more conveniently, of $\log A/C_1$ (figure 1). A corresponding experimental curve gives E as a function of $-\log C_1$, that is, a curve which could only coincide with one of the theoretical family of curves when $A = 1$. However, the shape of the curve will be determined (for a given ratio C_1/C_2) by U_c/U_A and not by C_1 , so that in order to measure $\log A$ it is only necessary to determine how far the experimental curve must be moved along the abscissa in order to be brought into coincidence with one of the theoretical family of curves. The curve whose shape is identical with the experimental curve then defines U_c/U_A . The experimental curve therefore can be used to measure the effective charge A on the membrane and also the ratio U_c/U_A , which by comparison with the corresponding values for water gives a measure of the sieve action of the membrane. Experiments with salts having anions and cations of equal mobility in water, such as potassium chloride, indicate directly the magnitude of the sieve action.

In order, therefore, to use for cation determinations a membrane which follows the general theory of Meyer and Sievers and of Teorell, it is necessary to find materials having either a well-marked sieve action or else a high charge per unit volume. At the time, however, when this work was started, it was not realized that any such comprehensive theory was available, and attention was focussed on the sieve action alone. The

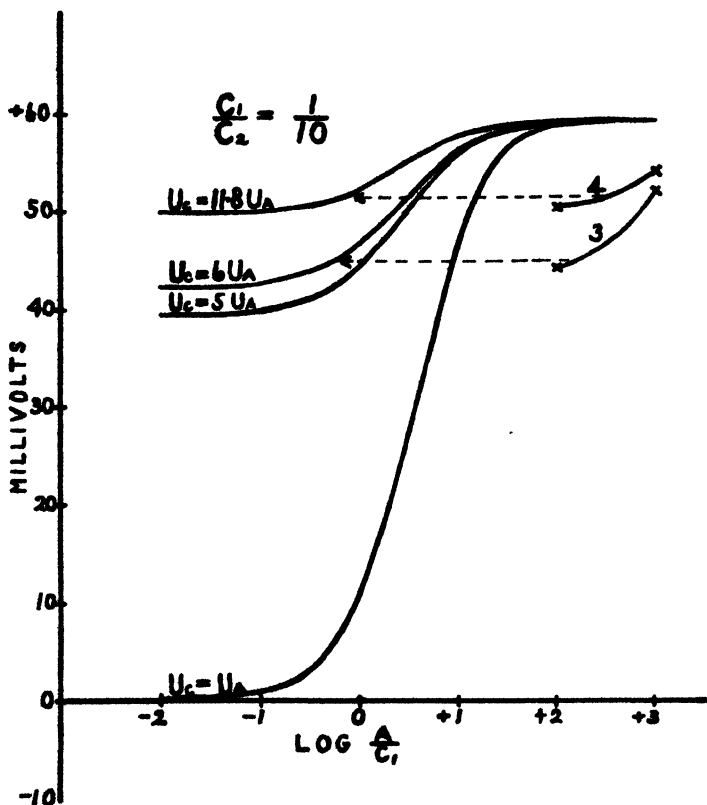


FIG. 1. Family of curves obtained by plotting potentials against $\log \frac{A}{C_1}$, in which $\frac{C_1}{C_2}$ is constant and U_2 and U_1 are varied; curves 3 and 4, results with apophyllite.

crystalline zeolites were chosen as promising well in this respect. Hangaard (2) has also pointed out the possibility of using base-exchange minerals.

II. EXPERIMENTAL

(a) Choice of materials

Few of the zeolites occur in crystals from which it is possible to grind plates free from cracks. A survey of the possibilities was much facilitated

by specimens from the Ashcroft Collection of the British Museum. The author is deeply indebted to Dr. M. H. Hey for his help in this matter. Chabazite and the closely related gmelinite were found to occur in some localities as small clear crystals, the best material having the habit of gmelinite. Plates up to about 4 mm. in diameter were prepared by grinding at right angles to the hexagonal axis. No other true zeolites were found suitable. Heulandite, which at first sight appears promising, since it occurs in large crystals with a good basal cleavage, is generally permeated with fine cracks.

Among the zeolite-like minerals which show some base-exchange properties, apophyllite has proved to be an excellent choice. Clear crystals can be obtained, and the basal cleavage is so good that several plates can be made from one perfect crystal. Such plates have ranged up to 12 mm. in diameter.

(b) *Preparation of electrodes*

The crystal or cleavage plate is ground down on a glass plate using grade FFF carborundum until about 1 mm. thick. It is then mounted in water or glycerol and examined microscopically for cracks. If satisfactory, it is ground further to about 0.5 mm. From here onwards the finest emery is used, fractionated in alcohol so as to include only particles $< 10 \mu$. Depending on the area of the plate, the final grinding is carried down to 0.1–0.3 mm. The plate is then mounted with deKhotinsky cement or Picein on the ground end of a glass tube. This is done very carefully over a small, steady flame. The crystal edges are finally coated while hot with the insulating cement. The membrane is then soaked for 3 to 10 days in a dilute salt solution, the choice depending on the experiments to be made subsequently. When measurements become possible, a standard solution of the chloride of the cation concerned is used inside the glass tube, along with a silver chloride electrode. The membrane dips into a beaker containing the second solution and a saturated calomel electrode.

(c) *Apparatus and technique*

A Leeds and Northrup thermionic amplifier^{*} was used in conjunction with a student type potentiometer calibrated to 0.1 millivolt. This apparatus gave good measurements with resistances up to 10^8 megohms.

The resistance of the membrane falls during the soaking period, and reproducible potentials are established only for values less than 1000 megohms. The asymmetry potential at first is often very high and it

^{*} The author is grateful to Dr. Wm. J. Robbins and Mr. F. Kavanagh for the facilities made available in the Department of Botany, where the earliest experiments were carried out by means of an amplifier built by Mr. Kavanagh. The Leeds and Northrup amplifier was purchased by a grant from the University of Missouri Research Council.

attains a constant low value only some days after measurements are first possible. The resistance falls suddenly when cracks develop in the crystal or cement. Neither deKhotinsky cement nor Picein is wholly satisfactory; the former is eventually attacked by water, and the latter is prone to crack. Carefully prepared electrodes can sometimes be used for 2 months without recementing. Control experiments indicated that the current was not being carried along minute cracks between the cement and the crystal or the glass tube. Membranes sometimes show unsuspected cracks which extend only part way through the plate. These cause a slow attainment of equilibrium on changing the concentration of the outer or inner solution. With a good membrane, equilibrium is established quickly, except when the cation exchange between crystal and solution causes disturbances. This can be avoided by soaking.

TABLE 1
Potential differences with chabazite membranes

ELECTRODE NO.	INNER SOLUTION	$\frac{N}{10,000} - \frac{N}{1000}$	$\frac{N}{1000} - \frac{N}{100}$	$\frac{N}{100} - \frac{N}{10}$
		<i>millivolts</i>	<i>millivolts</i>	<i>millivolts</i>
1.....	N/10 KCl		40.5	49.4
	N/100 BaCl ₂		24.9	24.4
	N/100 CaCl ₂		28.7	22.1
	N/10 LiCl		8.3	41.8
	N/10 KCl		39.3	48.9
3.....	N/100 KCl	19.6	41.9	47.6
	N/1000 HCl	56.3	49.5	
	N/100 KCl	38.1	51.3	51.3
	N/100 CaCl ₂	23.2	21.8	
	N/100 (triton B)Cl	17.6	27.5	32.7

In making the measurements, after two or three orientation settings, the outer solution was replaced by fresh, and three more readings were taken. In the absence of drift the mean of these was adopted; otherwise the process was repeated until constancy was attained. The potential using the same solution inside and outside was taken as the zero; during a series of measurements the inner solution was kept constant and the outer solution varied in steps of 10 or 1/10. The potentials reported are the differences between these values and the zero value.

III. RESULTS WITH CHABAZITE, $(\text{Ca}, \text{Na}_2)\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$

Table 1 gives two series of results with chabazite membranes. The values are corrected to 25°C. in this and all other tables. The experiments are reported in the order in which they were carried out.

The results clearly indicate that chabazite membranes do not follow the behavior predicted on the basis of Meyer's theory, according to which, for a given ratio C_1/C_2 , the potential difference should decrease as the concentration increases. Only the divalent cations and hydrogen show this effect. The monovalent cations show an increase in potential as the concentration increases. This might be caused in two ways: (a) by hydrolysis of the mineral and (b) by an endothermic exchange reaction between monovalent ions in the outer solution and divalent exchangeable ions attached to the lattice. The fact that membrane 3 gave higher values for potassium chloride after being in contact with hydrochloric acid would suggest mechanism (a). The results with triton B chloride (benzyltrimethylammonium chloride) show that a sieve action restricting cations as well as anions operates when the cation is large. Surface ionic exchange, however, still provides a mechanism for a reduced cation conductance.

IV. RESULTS WITH APOPHYLLITE, $\text{KF} \cdot \text{Ca}_4\text{Si}_8\text{O}_{20} \cdot 8\text{H}_2\text{O}$

(a) *Monovalent cations*

The earlier experiments were concerned chiefly with the reproducibility of results and with changes in the membranes with time. Potassium chloride was the most suitable electrolyte for these studies. In the case of apophyllite it is absolutely necessary to coat the edges of the crystal plate with cement, otherwise the electrode shows successively diminishing potential differences. This peculiarity is to be ascribed to the mica-like crystal structure. The slit-like channels parallel to the silicon-oxygen sheets contain the calcium, potassium, fluorine, and water, and they are much larger in dimensions than the channels which pass through the silicon-oxygen sheets. In the best apophyllite membranes apparently the conductance is at right angles to the plane of the sheets, i.e., to the plane of cleavage. The deterioration of these membranes with time is probably due to penetration of the cement by water, since recementing restores the original properties. Table 2 illustrates these peculiarities. Successive experiments are given in consecutive lines.

Table 2 clearly shows that hydrolysis is perceptible only at very low concentrations. It is possible to use the $N/1000 - N/100$ and $N/100 - N/10$ results to determine graphically U_c/U_A and A (see figure 1). For membrane 3, $U_c/U_A = 6.0$ and $A = 2.95 \times 10^{-3}$. For membrane 4, $U_c/U_A = 11.8$ and $A = 1.78 \times 10^{-3}$. The values for U_c/U_A indicate a strong but variable sieve action. The ideal crystal structure would explain its strength, and departures from the ideal its variability. The low values for A indicate that thermodynamically only a very small fraction of the cations present can be regarded as dissociated. The total concentration of potassium in the lattice water would be about 7 N .

(b) *Divalent cations*

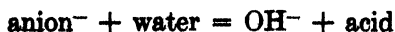
The theory of Meyer is applicable only to binary salts. For calcium chloride and similar salts the Donnan equations admit of no simple solution. In future work it would be well to use magnesium sulfate, to which the theory can apply. In table 3 the main feature reviewed is the effect of the anion on the potential differences with different calcium salts in the outer solution.

The choice of formate and acetate to compare with chloride was made on the basis of ionic mobilities; chloride is faster than calcium, formate

TABLE 2
Behavior of apophyllite membranes with monovalent cations

ELECTRODE NO.	TREATMENT	INNER SOLUTION	$\frac{N}{10,000} - \frac{N}{1000}$	$\frac{N}{1000} - \frac{N}{100}$	$\frac{N}{100} - \frac{N}{10}$
			millivolts	millivolts	millivolts
3.....	Edges bare	N/100 KCl		40.4	27.7
	Edges bare	N/100 KCl		25.4	13.7
	Edges coated	N/100 KCl	49.4	46.8	41.4
	Edges coated	N/100 KCl	50.3	53.3	41.3
	Edges coated	N/100 KCl	53.4	50.7	43.5
	Recemented	N/100 KCl	58.7	49.2	49.0
	Recemented	N/100 KCl	56.7	53.7	50.0
	Recemented	N/100 KCl	56.2	55.0	45.2
	Recemented	N/100 KCl	54.5	53.0	40.5
	Recemented	N/100 KCl	50.8	54.6	42.8
4.....	Edges bare	N/100 KCl		40.7	23.5
	Edges coated	N/100 KCl		51.9	47.5
	Edges coated	N/100 KCl	50.2	54.7	50.8
	Edges coated	N/100 KCl	53.2	54.0	52.1
	Edges coated	N/100 KCl	53.0	54.5	51.1
	Edges coated	N/100 KCl	55.0	55.6	51.3
	Edges coated	N/100 NaCl		52.6	52.3
	Edges coated	N/100 NaCl		52.7	51.3

is about equal, and acetate is slower. At the higher concentrations the order of the potentials is chloride > formate > acetate, which is the reverse of what would be expected from the mobilities in water. The behavior may possibly be explained by the relative ease with which the reaction



can proceed. It is assumed here that OH⁻ is the only mobile anion within the membrane. The very small potential given by calcium hydroxide solutions agrees also with this supposition. Separate experiments with

calcium acetate-acetic acid buffers showed that in the pH range 4 to 7 the pH had little influence on the potential differences of $N/100$ and $N/1000$ solutions.

V. THE MEASUREMENT OF UNKNOWN CATIONIC ACTIVITIES

The possibility of using membrane electrodes for the determination of cationic activities in true solutions and colloidal systems turns largely on the influence of the anion. Since it is hardly conceivable that any mem-

TABLE 3
Behavior of apophyllite membranes with divalent cations

ELECTRODE NO.	INNER SOLUTION	OUTER SOLUTION	$\frac{N}{10,000} - \frac{N}{1000}$	$\frac{N}{1000} - \frac{N}{100}$	$\frac{N}{100} - \frac{N}{10}$
			millivolts	millivolts	millivolts
4	$N/100 \text{ BaCl}_2$	Barium chloride	30.0	26.3	19.7
6	$N/100 \text{ CaCl}_2$	Calcium chloride	25.4	24.0	19.9
	$N/100 \text{ CaCl}_2$	Calcium formate	21.0	23.5	16.7
	$N/100 \text{ CaCl}_2$	Calcium acetate	24.1	23.9	15.1
7	$N/100 \text{ CaCl}_2$	Calcium chloride	21.2	23.8	22.4
	$N/100 \text{ CaCl}_2$	Calcium formate	25.0	23.9	19.7
	$N/100 \text{ CaCl}_2$	Calcium acetate	25.8	24.1	16.2
	$N/100 \text{ CaCl}_2$	Calcium hydroxide		6.5	

TABLE 4
Comparative pH values with glass and apophyllite membranes

INNER SOLUTION	OUTER SOLUTION	pH WITH GLASS MEMBRANE	pH WITH APOPHYLLITE MEMBRANE
$N/1000 \text{ HCl}$	$N/100 \text{ } p\text{-toluenesulfonic acid}$	2.07	2.00
$N/1000 \text{ HCl}$	$N/1000 \text{ } p\text{-toluenesulfonic acid}$	3.05	2.88
$N/1000 \text{ HCl}$	4 per cent H agar	2.37	2.23
$N/1000 \text{ HCl}$	0.4 per cent H agar	3.16	3.10

brane should act as a perfect cationic sieve, calibration with known salt solutions appears inevitable. It is then important to know whether the replacement of chloride by a polyvalent colloidal anion will affect the relative mobilities of anion and cation within the membrane. The experiments with various calcium salts would seem to indicate that the anions do not directly penetrate the apophyllite membrane, that is, anion conductance occurs probably by OH^- ions. The potential difference should be independent of the anion, except insofar as the interchange reaction between anion and water may involve different energy changes. Table 3

would indicate that from high dilutions to $N/100$ the differences are unimportant. Thus there is a reasonable prospect of obtaining a moderate degree of accuracy with membranes having a high sieve action, such as No. 4.

In order to test this point comparisons were made of hydrochloric acid and *p*-toluenesulfonic acid and also of hydrochloric acid and electro-dialyzed agar. $N/1000$ and $N/100$ hydrochloric acid solutions were used to calibrate the membrane and a glass electrode. Then comparable measurements were made, using two dilutions of *p*-toluenesulfonic acid (strong acid, large anion) and two dilutions of electro-dialyzed agar (weaker acid, colloidal anion). Owing to the attack by strong acids on the membrane, these measurements had to be carried out without previous soaking. In table 4 the pH values derived from the glass electrode measurements and the membrane measurements are compared.

The glass electrode measurements give somewhat higher values than apophyllite. This may perhaps arise from the attack on the mineral by the acid solutions. Unfortunately, it seems at present impossible to devise a similar check for metallic cations such as potassium and calcium which would be applicable to dilute solutions, but there is a better prospect for silver.

In view of the importance of cationic activity measurements in colloidal systems further work in this field is needed. It is unlikely that the same accuracy will be attained as is possible with the hydrogen electrode or that a membrane specific for one metallic cation only can be found. Nevertheless, our ignorance of cationic activities in such an important colloidal system as the soil is such that even a first approximation may be very helpful.

REFERENCES

- (1) ANDERSON, R. S.: J. Biol. Chem. **115**, 323 (1936).
- (2) HANGAARD, C.: Nature **146**, 66 (1938).
- (3) HOROVITZ, K.: Z. Physik **15**, 369 (1923); Z. physik. Chem. **115**, 424 (1925).
- (4) MEYER, K. H.: Trans. Faraday Soc. **33**, 1073 (1937).
- (5) MEYER, K. H., HAUPTMANN, H., AND SIEVERS, J. F.: Helv. Chim. Acta **19**, 948 (1936).
- (6) MEYER, K. H., AND SIEVERS, J. F.: Helv. Chim. Acta **19**, 649, 665, 987 (1936).
- (7) MICHAELIS, L.: Colloid Symposium Monograph **5**, 135 (1927).
- (8) SCHILLER, H.: Ann. Physik [4] **74**, 105 (1924).
- (9) TENDELOO, J. H. C.: J. Biol. Chem. **113**, 333 (1936).
- (10) TENDELOO, J. H. C.: J. Biol. Chem. **118**, 253 (1937).
- (11) THEORELL, T.: Proc. Soc. Exptl. Biol. Med. **33**, 282 (1935); Trans. Faraday Soc. **33**, 1054 (1937).
- (12) WILLERANDT, J.: J. Gen. Physiol. **18**, 933 (1935).

A STUDY OF BLOOD SERUM PROTEINS BY ELECTROPHORESIS¹

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The primary object of this investigation was to study the changes in the proteins of the blood serum and other related organs caused by various physiological conditions, and in this manner gain a better understanding of the nature of these proteins and of the mechanism by which they are stored and utilized by the body. In particular, the experiments here recorded study the changes in the blood serum proteins of the adult of one species brought about by the ingestion of colostrum from an animal of a different species. To study these changes salting-out and electrophoretic experiments have been used.

Famulener, Little, Smith, and others (1, 6, 9, 10) found many years ago that antibodies are transferred from the mother to its young by colostrum. The literature is well reviewed by Traum (14). Howe (2) and Orcutt and Howe (7) paralleled this work by observing a simultaneous increase in globulins. Recently Schneider and Szathmary (8) confirmed earlier results with experiments on a number of different species. These experiments have been extended by the authors by feeding cow's colostrum to man and to the adult rat with a resulting increase in globulin concentration.

This appreciable change in the blood serum proteins of the adult rat was first noted in 1936 by one of the authors during a study of the building up of serum globulins in the newborn and adult animals. It was evident when a comparison was made of the salting-out curves made from blood serum of adult rats fed a normal stock diet and from the serum of adult rats fed colostrum. The curve obtained from the serum of the latter showed a protein fraction which was not visible in the former.

The procedure used in these experiments has been fully described in a previous communication (3). To weighed portions of the serum dialyzed against a 5 per cent potassium citrate solution at pH 6.8, dry potassium

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citrate was added to make the desired salt concentration. The pH was maintained by added citric acid. The precipitated protein was separated on filters, and the liquid phase was analyzed for protein and potassium. All analyses were made on weighed samples. Processes were carried out as rapidly as possible at 0°C.

Figure 1 shows the curve from normal rat serum. The results were plotted as per cent by weight on Gibbs' triangular phase rule diagrams. Protein dried at 110°C., potassium citrate, and water are to be found at the apices of the triangles. Only a portion of the diagram is given, as may be seen from the percentages along its sides. The heavy line rep-

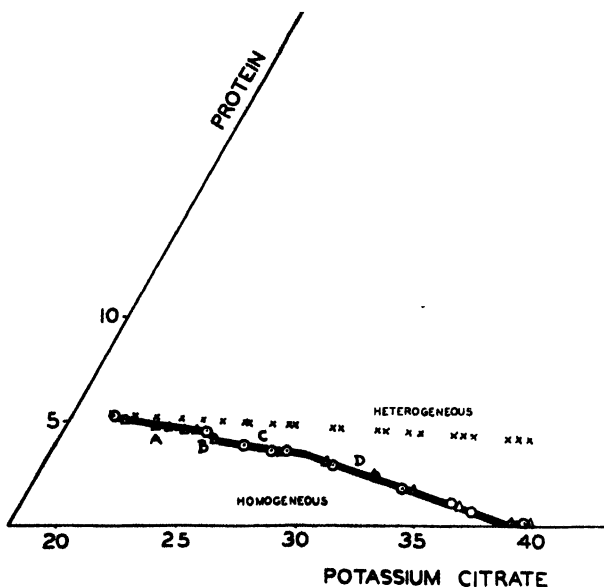


FIG. 1. Rat serum; stock diet. X, total composition; O, liquid phase; Δ, liquid phase

resents the analyses of the liquid phases in contact with the solid phases. A is considered the first fraction to appear as a solid phase on adding potassium citrate; B is precipitated on further addition, coming down in a very narrow range of salt concentration; and C is precipitated gradually as the salt concentration becomes higher. Finally D, the albumin fraction, appears.

In figure 1, the O's, and Δ's are experimental points on a line separating the liquid phase from the heterogeneous mixture. They were obtained from two different pools of blood serum, each from thirty stock male rats, 100 days old. They coincide. There are four fractions, as shown by the changes in direction of the curve with increasing amounts of potassium citrate.

In figure 2, also from serum of thirty male rats, 100 days old but colostrum-fed for 2 days, an extra change of direction occurs, showing the separation of another solid phase, C_2 .

Other proteins, such as casein, serum albumin, serum globulin, liver, and kidney, did not have this effect. After a 70 per cent protein diet of any of the above mentioned proteins is fed for 2 days, curves of the type found in figure 3 are found. This curve is made after feeding serum globulin.² The C_2 is missing or so small as to be negligible. Feeding of the dried colostrum³ for 2 days gave a curve in which C_2 is high but not as greatly increased as in the serum where fresh colostrum was used

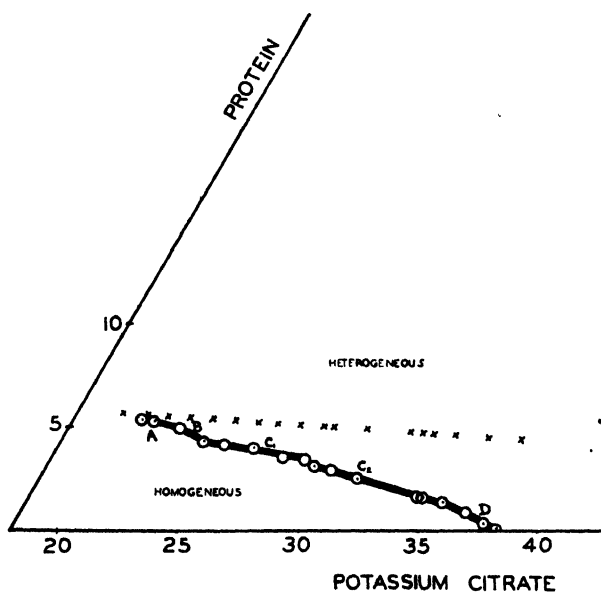


FIG. 2. Rat serum; diet of fresh cow's colostrum and milk for 2 days. \times , total composition; \circ , liquid phase

After 7 days' feeding of dried colostrum the presence of the unusual fraction is proportionately less and is somewhat masked by the great increase of C_1 . Figure 4 is made from such serum. This curve may be compared with those made from the serum of rats on other high-protein diets for the same length of time. In figure 5 the results are given after feeding a globulin diet for 7 days. The C_2 phase is still not very visible.

Electrophoretic study of the serum proteins, in serum both from stock rats and from those fed colostrum, was carried out in the Tiselius ap-

² Horse serum globulin was separated by half-saturation with ammonium sulfate, denatured, dried, and washed.

³ The colostrum was spray-dried without preheating.

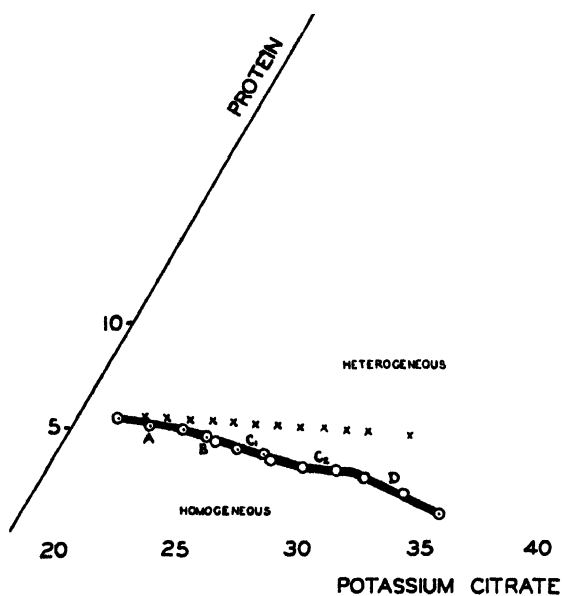


FIG. 3. Rat serum; diet of serum globulin for 2 days. X, total composition; O, liquid phase

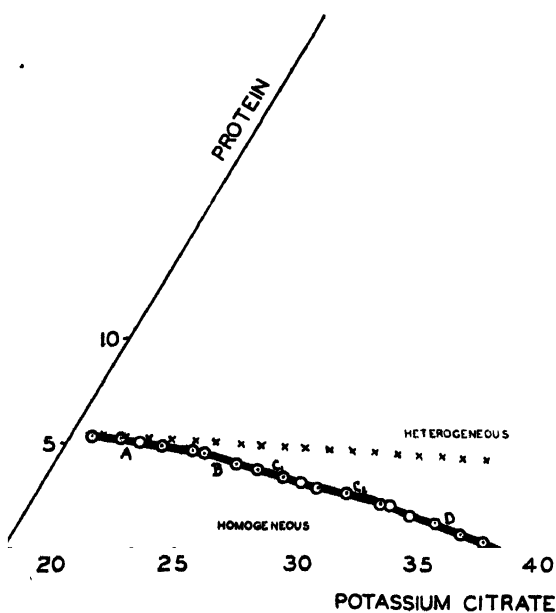


FIG. 4. Rat serum; diet of dried cow's colostrum for 7 days. X, total composition; O, liquid phase

paratus (11), using buffers 0.02 *M* in phosphate and 0.15 *M* in sodium chloride. Several pH values were used for the normal serum, but since it was found that the separation of the globulins is very satisfactory at a pH of 6.2, this value was used extensively. A potential gradient of 4.4 volts per centimeter was used in these experiments, since we had found that a higher voltage produces an increased number of protein fractions. This is probably due to the breaking of loose protein complexes by the application of a sufficiently high potential gradient (5).

The electrophoretic diagram for normal rat serum has been given by the authors in a previous article (5). In this communication it was

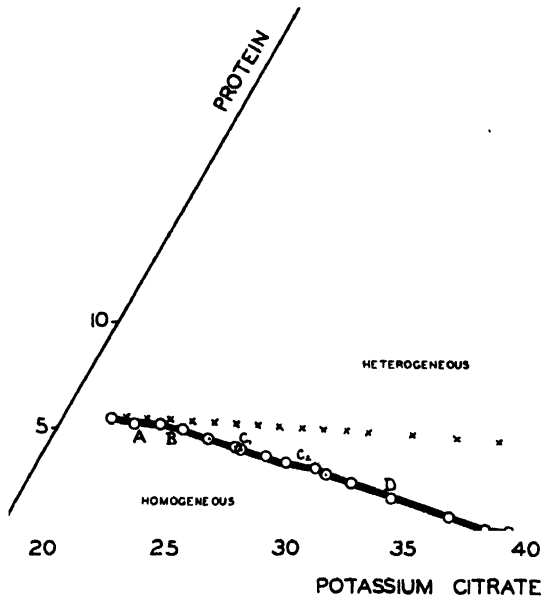


FIG. 5. Rat serum; diet of serum globulin for 7 days. X, total composition; O liquid phase

reported that normal rat serum yields only three protein fractions,—an albumin and two globulins that were identified with the α - and β -fractions found by Tiselius and coworkers in horse serum. Further investigation has shown that a third globulin fraction is present in the rat serum, and that its concentration is normally so low that the *Schlieren* band corresponding to this globulin is visible only when undiluted serum is used, and then only faintly. Thus, when the serum is diluted with buffer, as it usually is for electrophoretic determinations, this fraction seems to be absent. The globulin that occurs at low concentration corresponds to the α -fraction described by Tiselius, so that the two fractions previously reported as α and β are found to correspond to Tiselius' β and γ .

The serum from colostrum-fed rats shows the line corresponding to the α -globulin quite strongly, even in serum diluted 1 to 3 with buffer. This protein becomes a considerable portion of the total globulins after 24 hr. of feeding colostrum. This is, then, one of the changes that occur in rat serum, owing to the ingestion of colostrum. The increase in the concentration of one of the naturally occurring blood serum proteins is similarly found to occur in man. Eighty grams of dried colostrum, ingested during 2 days, noticeably increases the concentration of α -globulin in human serum. Figure 6 shows reproductions of electrophoretic diagrams, illustrating this effect in rat serum (diluted 1 to 3 with buffer) and human serum (diluted 1 to 4).

Tiselius (12) has found that the best source of the α -globulin in horse serum is the pseudoglobulin in which the γ -fraction also appears. This is comparable to the C-fraction of the salting-out curves. If this is also true for rat serum, and there are indications that it is, then the α -fraction may be the same fraction as the C_2 visible in the salting-out curves after

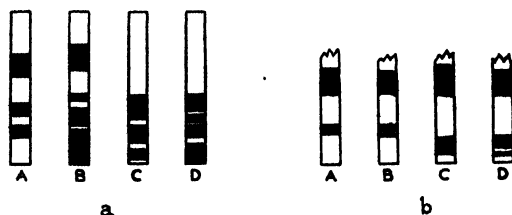


FIG. 6. (a) Electrophoretic diagrams showing increase in α -fraction. A and B, rat serum before and after ingestion of colostrum; C and D, human serum. (b) Electrophoretic diagrams showing division of the γ -fraction. A and B, rat serum; C and D, human serum.

2 days of feeding colostrum. Tiselius' β -fraction probably corresponds to our A-fraction.

A second and subsequent effect is the division of the γ -fraction or the appearance of a new protein fraction that has almost the same mobility as the γ -fraction in normal serum. The effect is somewhat similar to that obtained with immune sera. In immune horse serum, Tiselius and Kabat (13) found the γ -fraction to occur in two parts of rather different mobilities, so that a good separation of these two fractions was obtained. In the serum of colostrum-fed rats, the mobilities are more nearly the same; thus the separation becomes more difficult. At pH 7.0 the two fractions can not be separated, and the apparent effect is the increase in the concentration of the γ -globulin. In immune rabbit serum, this concentration change appears to be the only effect, since no pH value could be found at which the γ -fraction could be separated. Our experiments on immune rabbit serum confirmed in this respect the observations of Kabat. The immune rabbit serum was obtained from Dr. S. Raffel of the Department of Bacteriology of Stanford University.

Since it seemed advisable to compare the effect produced by the colostrum diet with any effect that immunization would have on the rat serum, the electrophoretic diagrams of serum of rats that had been made highly immune to *Proteus vulgaris* and to sheep red cells were obtained through the coöperation of Dr. S. Raffel. In each case a similar division of the fraction was observed. As has been shown above, the two main effects on the serum protein content caused by the ingestion of colostrum are the increase in the concentration of the α -fraction and the division of the γ -globulin. To determine which of these two effects is the one more directly connected with the presence of agglutinins in the rat serum, samples of serum rendered highly immune by infections of killed bacteria and sheep's erythrocytes were fractionated by electrophoresis, and each fraction titrated for agglutinin contents. In this manner it was found that the more rapidly moving part of the γ -fraction has the highest titer per gram of protein present. In no instance was the separation of the protein fractions absolutely complete, so that no samples containing a single protein fraction were titrated.

It should be possible to determine whether the γ -fraction is split or a new fraction has appeared by a more complete study of the mobilities. A pH will have to be found at which greater mobility and consequently more accuracy can be obtained in the study of the original γ -fraction and the two subsequent γ -fractions.

The idea occurred to the authors that the new fraction might have some relation to the antibodies, in view of the work of Famulener and others on antibodies in the newborn, Howe's and our own (4) on the increase in globulins in the newborn,—changes directly traceable to the ingestion of colostrum,—as well as the similarity of electrophoretic diagrams of immune sera and sera after the ingestion of colostrum. Experiments are still in progress to determine this point. In five cases agglutinins to *Brucella* have been found in adult rat serum in a dilution of 1 to 8 and less after feeding colostrum having a low antibody titre. The controls in each case were negative in all dilutions. In one case where the colostrum had a high titre to *Brucella* no agglutinins were found in that serum after its ingestion. Previously, sera of the newborn had been tested in dilutions of 1 to 10 or 1 to 20 and above. Since the mechanism of the process is doubtful, no explanation can be offered at present.

CONCLUSIONS

Changes in rat and human serum take place after feeding cow's colostrum. The α -fraction is greatly increased, while the γ -fraction is either split or a new fraction appears. The change in the number of fractions is visible both in the salting-out curves and by electrophoresis.

Similar changes in the γ -fraction occur in highly immune rat serum.

REFERENCES

- (1) FAMULENER, L. W.: *J. Infectious Diseases* **10**, 332 (1912).
- (2) HOWE, P. E.: *J. Biol. Chem.* **49**, 115 (1921).
- (3) JAMESON, E., AND ROBERTS D. B.: *J. Gen. Physiol.* **30**, 475 (1937).
- (4) JAMESON, E., AND ROBERTS, D. B.: *J. Gen. Physiol.* **21**, 249 (1937).
- (5) JAMESON, E., AND ALVAREZ-TOSTADO, C.: *Proc. Soc. Exptl. Biol. Med.* **40**, 476 (1939).
- (6) LITTLE, R. B., AND ORCUTT, M. L.: *J. Exptl. Med.* **35**, 161 (1922).
- (7) ORCUTT, M. L., AND HOWE, P. E.: *J. Exptl. Med.* **36**, 291 (1922).
- (8) SCHNEIDER, L., AND SZATHMARY, J.: *Z. Immunitäts.* **95**, 16, 177, 189 (1939).
- (9) SMITH, T., AND LITTLE, R.: *J. Exptl. Med.* **36**, 181 (1922).
- (10) SMITH, T., AND LITTLE, R.: *J. Exptl. Med.* **36**, 453 (1922).
- (11) TISELIUS, A.: *Trans. Faraday Soc.* **33**, 524 (1937).
- (12) TISELIUS, A.: *Biochem. J.* **31**, 1464 (1937).
- (13) TISELIUS, A., AND KABAT, E. A.: *J. Exptl. Med.* **69**, 119 (1939).
- (14) TRAUM, J: *Cornell Vet.* **13**, 135 (1923).

STUDIES OF SULFONATES. VI

THE EFFECT OF SODIUM CHLORIDE ON THE SOLUBILITY OF SODIUM DODECYLSULFONATE AND SODIUM TETRADECYLSULFONATE. THE SOLUBILITY AT 50°C. OF CALCIUM DODECYLSULFONATE AND CALCIUM DODECYL SULFATE IN AQUEOUS SOLUTIONS OF THE CORRESPONDING SODIUM SALTS¹

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The investigation reported in this paper is a continuation of the work in this laboratory on the solubilities of sodium alkylsulfonates. The previous work by Tartar and Wright (5) showed that as the temperature is increased there is an abrupt break in the solubility curve of these substances, from comparatively small values of solubility to high values. This sudden change was explained by assuming that the formation of micelles, as suggested by Hartley (1), begins at the concentration at which the break occurs.

Murray (2) has discussed the effect of potassium chloride on the solubility of potassium cetylsulfonate and has shown that the Krafft point³ is raised by the addition of potassium chloride.

Numerous investigators have reported qualitative findings indicating that calcium salts are more soluble in solutions of sodium alkyl sulfates than in water alone. The increase in the solubility of calcium salts is of great importance in the use of alkyl sulfates as detergents.

The results reported in this paper were obtained from a study (a) of the solubility of sodium dodecyl- and tetradecyl-sulfonates in solutions of sodium chloride and (b) of the solubility of calcium dodecyl sulfate and calcium dodecylsulfonate in solutions of the corresponding sodium salts.

APPARATUS AND MATERIALS

The sodium dodecylsulfonate and sodium tetradecylsulfonate were portions of material used by Tartar and Wright (5). The sodium dodecyl sulfate was prepared by Reed (3). Sodium laurate was made from

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² Standard Oil Company of California Fellow, 1938-39.

³ Temperature above which the substance is exceedingly soluble.

lauric acid (m.p. 42–43°C.) obtained from the Eastman Kodak Company. The acid was carefully neutralized with sodium carbonate and extracted with ether.

The calcium salts were obtained by adding a solution of calcium chloride to solutions of the corresponding sodium salts. The precipitated calcium salts were first washed on a filter. Complete removal of the calcium chloride was finally accomplished by repeated washings by thorough shaking with water in a 2-liter, glass-stoppered Pyrex bottle. The salts were then

TABLE 1

Solubility of sodium dodecylsulfonate and sodium tetradecylsulfonate in sodium chloride solutions

SODIUM DODECYLSULFONATE			SODIUM TETRADECYLSULFONATE		
Temperature	Concentration	Molality	Temperature	Concentration	Molality
Sodium chloride solution = 0.004 molal					
°C.	grams per 100 g. H ₂ O		°C.	grams per 100 g. H ₂ O	
28.0	0.166	0.00610	28.0	0.0126	0.000420
31.0	0.202	0.00743	30.0	0.0171	0.000570
33.0	0.233	0.00857	33.0	0.0204	0.000680
35.0	0.305	0.0112	35.0	0.026	0.000867
36.0	0.623	0.0230	40.0	0.047	0.00168
			41.5	0.0503	0.00168
			43.0	0.0565	0.00188
			44.6	0.175	0.00583
			46.0	0.662	0.0221
Sodium chloride solution = 0.008 molal					
25.0	0.110	0.00404	35.0	0.0110	0.000368
30.0	0.157	0.00577	40.0	0.0276	0.000920
33.5	0.205	0.00754	43.5	0.059	0.00197
35.0	0.246	0.00904	44.0	0.083	0.00277
36.0	0.348	0.0128	46.0	0.346	0.0115

dried at 70°C. and analyzed. All analyses checked closely with the theoretical values.

The sodium chloride was of Merck's reagent quality. It was further purified by precipitating it twice by saturating its aqueous solution with hydrogen chloride; it was finally dried to constant weight.

The stock solutions of sodium chloride, sodium dodecylsulfonate, and sodium dodecyl sulfate were made on a weight basis.

The apparatus and procedure employed were similar to those used by Wright and Tartar (5). The only change was the use of a mercury seal instead of a capillary tube at the top of the vessel to prevent evaporation

of water. Equilibrium was approached from both the supersaturated and the unsaturated states; this was usually accomplished within 2 to 4 days. The excess of solid calcium salt was kept small to minimize any error due to the possible leaching of an impurity. The weighed samples of the saturated solutions were evaporated to dryness at 70°C. The weight of the calcium salt was determined by subtracting that of the sodium salt present in the solution.

SOLUBILITIES IN SODIUM CHLORIDE SOLUTIONS

The data for the solubility of sodium dodecylsulfonate and sodium tetradecylsulfonate in 0.004 and 0.008 molal sodium chloride are given in table 1 and presented graphically in figure 1. The temperatures are accu-

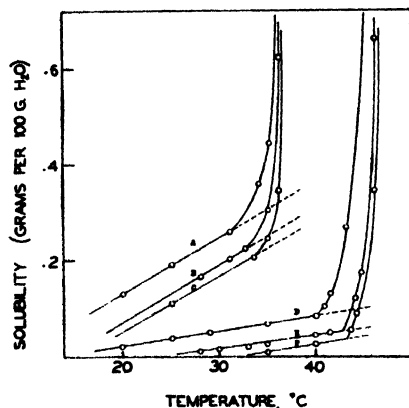


Fig. 1. Solubility of sodium alkylsulfonates in water and in sodium chloride solutions. Curves A, B, and C represent the solubility of sodium dodecylsulfonate in water, in a 0.004 molal solution of sodium chloride, and in a 0.008 molal sodium chloride solution, respectively. Curves D, E, and F represent the solubility of sodium tetradecylsulfonate in the corresponding solutions.

rate to 0.05°C. The curves for the solubilities of these sulfonates in water alone are taken from the work of Wright and Tartar.

The results show that the breaks in the solubility curves shift toward higher temperatures and lower concentrations as the concentration of sodium chloride is increased.

The solute is a mixture of uni-univalent molecules in a neutral solution and below the break exists as ions or simple ion pairs (molecules). The abrupt rise in the solubility of the sulfonate can be explained as being due primarily to the aggregation of the hydrocarbon chains in the form of ionic micelles containing ions and molecules.

The influence of sodium chloride on the solubility of the sulfonates below the concentration at which micelles are formed can be shown to be due to

the common-ion effect. Using the well-known equation of the Debye and Hückel theory for the activity coefficient of an electrolyte in varying solutions of different ionic strengths

$$\ln f_{\pm} = -z_+ z_- \frac{e^2}{(DkT)^{3/2}} \sqrt{\frac{\pi N}{1000} \sum c_i z_i^2}$$

the ion activity product for the saturated solution of either of the sulfonates can be calculated for its solutions at a given temperature. For example, the calculated ion activity products of sodium dodecylsulfonate in water, in 0.004 *N* sodium chloride, and in 0.008 *N* sodium chloride are 4.06, 3.55, and 3.85×10^{-5} , respectively. Considering the nature of these systems in which non-Coulombic forces play a large rôle, the experimental errors of the solubility determinations (near 1 per cent), and the assumptions involved in the theoretical treatment, the data are in satisfactory agreement and show quite clearly that the mass action law holds for this region. In a similar manner it can be shown that the activity product of a given sulfonate at the concentration at which micelles form is essentially the same, disregarding the limited variation in temperature, in the different solutions, within the limits of experimental error and theory.

SOLUBILITY OF CALCIUM DODECYLSULFONATE AND OF CALCIUM DODECYL SULFATE

The data on the solubility of calcium dodecylsulfonate in aqueous solutions at 50°C. are reported in table 2. The values for the solubility of this salt in water agree well with those found by Reed and Tartar (4). The relation of the solubility of calcium dodecylsulfonate to the concentration of the sodium salt is shown in figure 2; a portion of the curve drawn to larger scale will be found in figure 3.

The initial lowering of the solubility of calcium dodecylsulfonate by small concentrations (below the critical concentration for the formation of micelles) can be accounted for upon the basis of the common-ion effect, using the Debye and Hückel equation for the calculation of the activity coefficients of the ions.

The minimum of the curve occurs at a concentration of the sodium salt below that at which micelles form in solutions of this substance alone, at a lower temperature, *viz.*, 0.0125 *M* at 35°C. (5). The increased solubility of the calcium salt at the higher concentrations (beyond the minimum) can be explained as follows: There are present sulfonate, calcium, and sodium ions. The paraffin chain ends of the sulfonate ions tend to aggregate in the form of a micellar multivalent anion; this tendency is opposed by the Coulombic forces of negatively charged polar sulfonate ends. The calcium ion, because of its greater valence, is held more readily as a gegen ion at the surface of such a micelle than the sodium ion, thus reducing the

repelling action of the negative charges. This complex ionic micelle with both calcium and sodium gegen ions should be more stable than if it were produced with the same number of paraffin chains from the sodium salt only; consequently it can be produced at lower concentrations.

TABLE 2

Solubility of calcium dodecylsulfonate and calcium dodecyl sulfate in solutions of the corresponding sodium salts at 50°C.

SODIUM DODECYLSULFONATE		CALCIUM DODECYLSULFONATE		SODIUM DODECYL SULFATE		CALCIUM DODECYL SULFATE	
Concentra- tion	Molality	Concentra- tion	Molality	Concentra- tion	Molality	Concentra- tion	Molality
<i>grams per 100 g. H₂O</i>		<i>grams per 100 g. H₂O</i>		<i>grams per 100 g. H₂O</i>		<i>grams per 100 g. H₂O</i>	
0.0	0.0	0.0220	0.000408	0.0	0.0	0.261	0.00457
0.0125	0.000460	0.0166	0.000308	0.200	0.00694	1.25	0.0219
0.0300	0.00110	0.0067	0.000124	0.600	0.0208	2.60	0.0455
0.1000	0.00368	0.0028	0.0000520	1.250	0.0434	4.30	0.0753
0.2000	0.00735	0.0043	0.0000798	2.500	0.0868	7.27	0.1273
0.6000	0.0220	0.0280	0.000482				
1.5000	0.0552	0.135	0.00250				
2.5000	0.0919	0.171	0.00317				
5.000	0.184	0.260	0.00482				
10.000	0.368	0.440	0.00816				
15.000	0.551	0.820	0.0152				

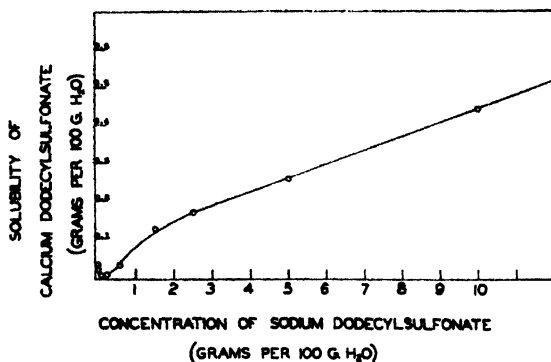


FIG. 2. The solubility of calcium dodecylsulfonate at 50°C. in solutions of sodium dodecylsulfonate.

The increase in the solubility of the calcium salt is accompanied by an increase of both calcium and sodium ions and a decrease of sulfonate ions in solution. The solid calcium sulfonate dissolves to satisfy its ion activity product in the saturated solutions.

With the change of the ratio of calcium to sodium ions in solution at the

various higher concentrations there would be a change in the relative amounts of these held as gegen ions. This might affect the surface charge of the micelle and possibly its constitution.

The results from the determination of the solubility of calcium dodecyl sulfate in aqueous solutions of sodium dodecyl sulfate are reported in table 2 and figure 4. The curve differs from that for the corresponding sulfonates in that there is no minimum. The solubility of calcium dodecyl sulfate in water at 50°C. is more than ten times that of the corresponding sulfonate. The saturated solution of the sodium dodecyl sulfate evidently must contain a considerable quantity of this substance in the form of micelles, and the addition of the sodium salt results in a greater solubility

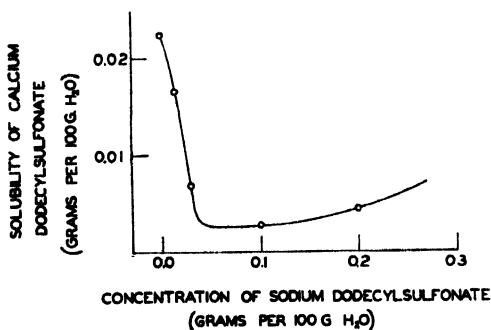


FIG. 3

FIG. 3. A magnification of the lower region of the solubility curve of calcium dodecylsulfonate in solutions of sodium dodecylsulfonate.

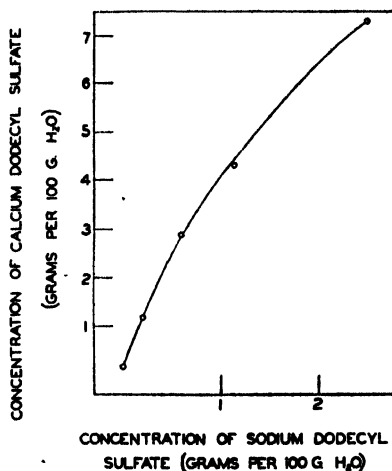


FIG. 4

FIG. 4. The solubility of calcium dodecyl sulfate at 50°C. in solutions of sodium dodecyl sulfate.

of the calcium, owing to complex micelle formation effects analogous to those presented above for the corresponding sulfonates.

SOLUBILITY OF CALCIUM LAURATE

The solubility of calcium laurate in solutions of sodium laurate was too small to be determined by the methods employed. Even concentrated solutions of the latter substance gave no measurable effect.

SUMMARY

1. The influence of sodium chloride on the solubility of sodium dodecyl-sulfonate and sodium tetradecylsulfonate at 50°C. has been determined.

Sodium chloride decreases the solubility, owing to the common-ion effect; it also increases the temperature and decreases the concentration at which micelles begin to form.

2. The solubilities of calcium dodecylsulfonate, calcium dodecyl sulfate, and calcium laurate in solutions of the corresponding sodium salts at 50°C. have been determined and discussed from the standpoint of complex micelle formation.

Grateful acknowledgment is made for a fellowship grant of funds from the Standard Oil Company of California, which made this investigation possible.

REFERENCES

- (1) HARTLEY: *Aqueous Solutions of Paraffin-Chain Salts*. Hermann et Cie., Paris (1936).
- (2) MURRAY: *Trans. Faraday Soc.* **31**, 199 (1935).
- (3) REED AND TARTAR: *J. Am. Chem. Soc.* **57**, 570 (1935).
- (4) REED AND TARTAR: *J. Am. Chem. Soc.* **58**, 322 (1936).
- (5) TARTAR AND WRIGHT: *J. Am. Chem. Soc.* **61**, 539 (1939).

EFFECT OF IONS OF THE LYOTROPIC SERIES ON THE INFRARED ABSORPTION SPECTRUM OF WATER¹

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No completely satisfactory explanation of the lyotropic series of ions has been proposed. It is logical to seek an explanation of the various lyotropic phenomena in the effects of the ions upon the dispersing medium or solvent. In view of the ideas concerning the structure of water based upon x-ray data (4), it is to be expected that the addition of ions of various radii and various energies of interaction should alter the infrared absorption bands found in water. Since the $3\ \mu$ (3400 cm.^{-1}) absorption band is the result of the hydrogen bonding of the water molecules (2), it is probable that changes in the infrared absorption will occur on the addition of various ions. These changes may be an alteration of the absorption coefficient, or a shift in the frequency of the position of maximum absorption, or an alteration of the curve of the absorption coefficient plotted against the wave length. Kujumzelis (3) finds an alteration in both the shape and the height of the Raman band of water at 3400 cm.^{-1} on the addition of various ions. The difficulties of the Raman technique do not lead to great accuracy, but nevertheless he is able to obtain direct evidence of a specific ion effect.

Inasmuch as Suhrmann and Breyer (5) have found that dissolved salts alter the infrared combination and overtone absorption bands of water up to $2.3\ \mu$ (4350 cm.^{-1}), it is to be expected that the same effects will be apparent on the shifted fundamental O—H radial frequency absorption band at $3\ \mu$ (3400 cm.^{-1}).

With this in mind we have studied the influence of several salts on the $3\ \mu$ liquid water absorption band. In order to compare the absorption we have computed the molecular absorption coefficient (in mm.^{-1}) by means of the following expression:

$$K_{\text{mm.}^{-1}} = \frac{18}{(\rho_{\text{solution}} - 0.01d) \times 1000 \times L_{\text{mm.}}} \cdot \log I_1/I_2$$

¹ Presented at the Sixteenth Colloid Symposium, held at Stanford University, California, July 6-8, 1939.

- where K = molecular absorption coefficient in mm.^{-1} ,
 $L = L_1 - L_2$, where L_1 and L_2 are thicknesses in millimeters of cells 1 and 2,
 I_1 = intensity of infrared radiation through cell 1 (galvanometer deflection),
 I_2 = intensity of infrared radiation through cell 2 (galvanometer deflection),
 ρ_{solution} = density of solution, and
 d = weight in grams of solute in 100 ml. of solution.

The films used in this investigation are between 0.004 and 0.0008 mm. thick. The greatest source of error is the determination of this film thickness. The films are produced by submerging the two fluorite plates of each cell in the solution to be measured, pressing the plates together without spacers, coating the edges of the plates with beeswax, and clamping in the cell holder. After various time intervals, at constant temperature, the thicknesses are estimated by an interferometric method (6). The method is capable of accuracy, but at such small thicknesses the irregularities inherent in the fluorite plates, which are plane to $\frac{1}{2}$ wave length of 5461 Ångström light, as well as the strains and stresses produced by waxing the plates together, make it difficult to measure thicknesses to 0.0002 mm. It is necessary to measure the thickness to this value because of the enormous absorption of water in the 3400 cm.^{-1} region.

The use of two cells of two different thicknesses allows the absorption to be measured without the complication of reflection at the fluorite-liquid and liquid-fluorite interfaces.

The infrared absorption is determined with a prism spectrometer, as previously described (1).

The average values of the molecular absorption coefficients at the peak of absorption and the position of the peaks are given in table 1.

It is interesting to note that the effect of the halogen anions upon the molecular absorption coefficient of water is in a lyotropic sequence parallel with the respective halogen ionic radii. The nitrate and thiocyanate ions seem to be in positions that are more difficult to explain. It is necessary to remember, however, that there are two opposing effects of the dissolving of an ion on the water molecules. These two effects are a depolymerization of the liquid structure and an electrostatic orientation of water molecules around the dissolved ion. The depolymerization of the liquid structure should leave the OH dipole more capable of vibrating at its fundamental frequency and consequently should increase the absorption. The orientation of water molecules around the ions should have the opposite effect.

The absorption of a viscous solution of calcium chloride, about 6 molar, has been compared with that of double-distilled water in the 3μ region.

The concentrated solution of calcium chloride was used in the hope that the highly hydrated calcium chloride might sufficiently depolymerize the water molecules so that some evidence of the fundamental OH radial frequency at 2.67μ or at slightly perturbed wave lengths might be found. As the curves in figure 1 show, there is a shift and broadening of the curve on the low wave length (2.67μ) side.

TABLE 1

Molecular absorption coefficients and wave lengths of peaks of absorption

CONCENTRATION	SALT	MOLECULAR ABSORPTION COEFFICIENT	WAVE LENGTH OF PEAK
<i>moles per liter</i>		<i>mm.⁻¹</i>	<i>μ</i>
1	KSCN	6.20	2.905
1	KCl	6.98	2.947
1	KNO ₃	7.72	2.904
	H ₂ O	7.86	2.897
1	KBr	8.07	2.905
1	KI	8.47	2.904

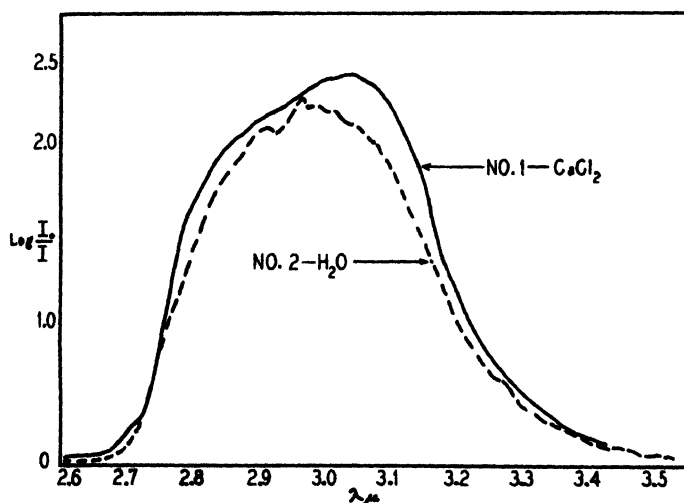


FIG. 1. Comparison of the infrared absorption spectrum of a viscous solution of calcium chloride with that of water.

We propose to continue this study along the following lines: (1) In order to increase the accuracy of thickness measurements we shall attempt to use the infrared spectrometer as an interferometer which should give measurements of thickness under conditions identical with those for the infrared absorption. (2) Similar studies are anticipated in the 6μ and 20μ

regions, where the angular mode of vibration and the hindered rotation frequencies occur. (9) Infrared reflection studies are contemplated in order to obviate the difficulties of thickness measurement.

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REFERENCES

- (1) BUSWELL, A. M., DEITZ, V., AND RODEBUSH, W. H.: J. Chem. Phys. **5**, 501 (1937).
- (2) ERRERA, J.: J. chim. phys. **34**, 617 (1937).
- (3) KUJUMZELIS, TH. G.: Z. Physik **110**, 742 (1938).
- (4) MORGAN, J., AND WARREN, B. E.: J. Chem. Phys. **6**, 666 (1938).
- (5) SUHRMANN, R., AND BREYER, F.: Z. physik. Chem. **B20**, 17 (1933).
- (6) WOOD, R. W.: Physical Optics, 3rd edition, p. 192. The Macmillan Company, New York (1934).

SURFACE MIGRATION OF IONS AND CONTACT EXCHANGE¹

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INTRODUCTION

Since the days of Quincke and Helmholtz, the concept of the electrical double layer surrounding colloidal particles has furnished qualitative and quantitative explanations of a variety of colloid chemical phenomena. It has been particularly successful in the elucidation of electrokinetic behavior and colloid stability. In the present paper some further consequences of the double layer theory are developed with special reference to the migration of ions in colloidal systems.

In calculations involving the electric double layer it is customary to assume for the colloidal particles a uniform surface charge. However, for the presentation and future theoretical interpretation of the phenomena reported here, the configuration of the attraction centers and the distances between them as conditioned by the crystal lattice pattern of the micelle are important. To each charge or ion constituting the inner layer belongs an oppositely charged counter ion. The latter is not held rigidly. On account of thermal agitation it oscillates over distances corresponding to the thickness of the outer sheet of the electrical double layer. The space to which the adsorbed ion is confined has been termed its "oscillation volume." This concept of the oscillation volume, which was used by Jenny (8) in developing a kinetic theory of base exchange, is in no way inconsistent with the diffuse double layer theory of Gouy and others who assume a uniform surface charge, but it acquires a special significance in those cases where the attraction spots on the colloidal surface are irregularly distributed, far apart, or of opposite sign.

Whenever a free ion enters the oscillation volume of an adsorbed ion, conditions for ion exchange are given and the ions may exchange places. The outgoing ion becomes a free, wandering ion, whereas the ingoing ion becomes an adsorbed ion. This process is known as *ion exchange* or *exchange adsorption*. It is schematically represented in figure 1. Nu-

¹ Presented at the Sixteenth Colloid Symposium, held at Stanford University, California, July 6-8, 1939.

merous empirical (6), thermodynamic (13), and kinetic (8) equations have been formulated for this process, which is common for clays, proteins, soaps, metallic sols, and probably all particles carrying electric charges.

MIGRATION OF IONS ON SURFACES

In figure 1 the surface conditions are such that the oscillation volumes are independent of each other. If the adsorption centers are relatively close together, or if the exchangeable ions are very loosely held, the oscillation spaces may overlap. Ions may then interchange on the same surface. By "exchange jumps" from one spot to another the ions may travel along surfaces (figure 2). The presence of solution ions is not necessary.

It is commonly believed that electrolytes diffusing through a membrane must travel in the pores essentially as ion pairs. The concept of surface migration indicates an additional mode of diffusion which involves only

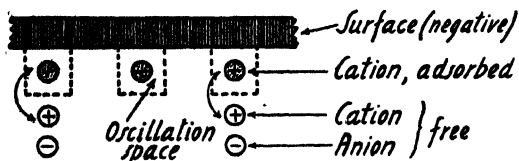


FIG. 1

FIG. 1. Model of base exchange or ionic exchange

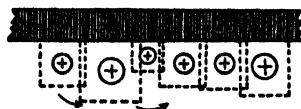


FIG. 2

FIG. 2. Schematic representation of migration of positive ions on a negative surface

one ion partner of the electrolyte, namely, the one carrying an opposite charge to the surface. The phenomenon is particularly striking when one of the electrolyte partners is too large to penetrate the pores. For negatively charged porous bodies like chabazite and permutite, which possess pores of 3 to 5 Å. radius and which have pronounced cation exchange, Wiegner and Cernescu (2) showed that electrolytes with large cations (e.g., tetramethylammonium chloride) cannot replace calcium ions from the interior of the gel because of restricted pore size. On the other hand, we observed no such reduction when the exchanging electrolyte consisted of a relatively small cation but a large anion (e.g., potassium citrate). Although the electrolyte as such could not enter the gel, cation replacement readily occurred, probably as a consequence of surface migration.

CONTACT EXCHANGE BETWEEN COLLOIDAL PARTICLES

The idea of overlapping oscillation volumes may be extended to transfer of ions from one colloidal particle to another. It is only necessary that

the two surfaces come close enough together so that the oscillation spaces intermingle. This corresponds to the condition of partial penetration of the electrical double layers of two colloidal particles. In sols this may result from Brownian movement; in gels, the structural arrangement may provide the necessary contact zones (figure 3). A search in the literature revealed that Cotton and Mouton (3) had foreseen the existence of contact exchange as early as 1906. For, in their book *Les Ultra-microscopes*, page 164, they make the brief remark: "Les échanges qui en résultent entre la micelle et le liquide ou entre deux micelles distinctes," Duclaux (5) and others have discussed the movement of adsorbed molecules on surfaces. Duclaux also has inferred certain consequences of interpenetration of diffuse ionic double layers in regard to the diffusion of ions in gels and the osmotic pressure of colloidal systems (4). He assumed extensive mixing of double layers, which, as Schofield (12) has shown, is not the case with clay systems.

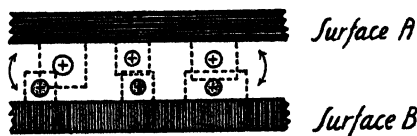


FIG. 3

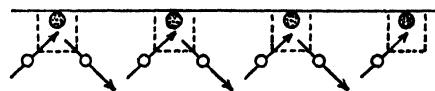


FIG. 4

FIG. 3. Model of contact exchange. The oscillation volumes of the adsorbed ions of particles A and B partially interpenetrate and the ions exchange places.

FIG. 4. Example of diffusion of ions in gels

The combination of surface migration and contact exchange provides an important mode of migration of ions in gels. Inasmuch as the surfaces are anisotropic, it will very likely be necessary to introduce directional diffusion coefficients. Generally speaking, the movement of ions in gels and sols may be divided into the following groups: (a) Free diffusion of ion pairs in the intermicellar pores and channels. (b) Adsorption of ions by colloidal particles which themselves diffuse as a result of Brownian movement or with the aid of some transporting agent (e.g., protoplasmic streaming in plant cells). (c) Stepwise exchange of ions between surfaces and intermicellar liquids as indicated in figure 4. (d) Surface migration and contact exchange, independent of the nature of the intermicellar liquid.

It is of course possible that all four types of mechanisms are operating in a given gel. The type of colloidal system is immaterial, provided the particles are capable of ion adsorption. If positive as well as negative spots are on the surface, both anions and cations may travel on the surfaces. Brooks (1) proposed for the diffusion of ions in protoplasm a similar chain of exchange reactions, without, however, giving a detailed picture of the mechanism involved, or experimental data in support.

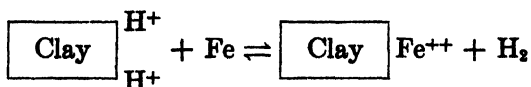
EXPERIMENTAL DATA

A study of contact exchange was begun early in 1936 by E. Winters (14) in the senior writer's laboratory. The experiments were confirmed and extended by R. Overstreet. At first only colloidal clay systems were investigated; later on the work was extended to include the important phase of plant root-soil relationships. A few typical illustrations only will be given here.

Studies on bentonite clays

Electrodialyzed clays exhibit the so-called suspension effect, that is, the pH of the suspension is much lower than that of the intermicellar liquid. The pH of the sol may be as low as 2, whereas the supernatant liquid (after centrifuging) may have a hydrogen-ion concentration corresponding to $\text{pH} = 6.5\text{--}7.0$. These findings indicate that practically all of the hydrogen ions are assembled on the surface of the clay particles.

An iron nail was pushed into a thick hydrogen bentonite gel containing a small amount of potassium ferricyanide as indicator for ferrous ion. Gas bubbles developed around the nail and the white color of the gel turned blue. The reaction may be written as follows:



Prior to insertion of the nail, a stream of nitrogen gas was passed through the gel for 3 days in order to remove carbon dioxide and oxygen. The same result was obtained when the indicator was added at the end of the experiment. Inasmuch as the intermicellar liquid, after dilution of the gel and subsequent centrifuging, did not show any test for ferrous ion, it is reasonable to assume that the diffusion of iron through the gel occurred by way of surface migration.

Iron hydrogen bentonite was prepared by treating hydrogen bentonite with normal ferrous sulfate. The resulting iron hydrogen clay was then leached with distilled water until the intermicellar liquid gave no test for ferrous ion. The sensitivity of the potassium ferricyanide test was found to be in the neighborhood of 1 part of ferrous ion per million.

A thick iron hydrogen bentonite suspension was placed in centrifuging tubes and centrifuged to a rigid gel (9.62 per cent). The supernatant liquid was poured off. Gels of hydrogen bentonite (pH about 3.5), potassium bentonite, and sodium bentonite (pH about 6.6) were placed directly over the iron hydrogen gel, as illustrated in figure 5.

The tubes were stoppered and allowed to stand for 1 week. Then 0.5 cc. distilled water, 3 drops of normal potassium ferricyanide reagent, and 1 drop of dilute hydrochloric acid were added to each tube to develop

the ferrous ion test. A very pronounced migration of ferrous ion was noticed in all cases, especially in hydrogen bentonite, extending about 0.5 cm. above the boundary of the two gels. The iron hydrogen bentonite underlying the sodium bentonite was analyzed for sodium. Knowing the amount of iron hydrogen bentonite and its cation adsorption capacity (100 milliequivalents per 100 g.), it could be calculated that 26 per cent of the adsorption centers of the iron hydrogen bentonite were now occupied by sodium.

One might contend that iron does not migrate by contact exchange but diffuses within the pores as $\text{Fe}(\text{OH})_2$ or possibly as $\text{Fe}(\text{HCO}_3)_2$ in amounts too small to be detected by the indicator. If this were the case, iron also should pass from one gel to another through a thin layer of water. Several experiments were designed to test this possibility.

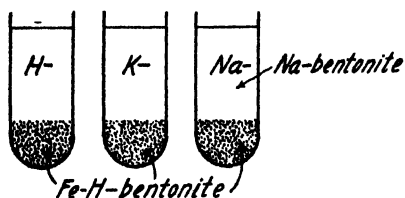


FIG. 5

FIG. 5. Experimental arrangement for the demonstration of diffusion of ferrous ion from iron hydrogen bentonite into hydrogen bentonite, potassium bentonite, and sodium bentonite.

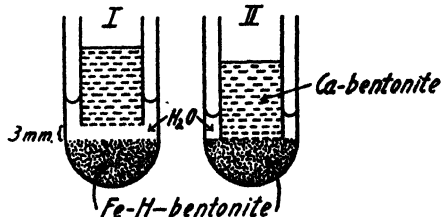


FIG. 6

FIG. 6. Ferrous iron migrates into calcium bentonite if the two gels are in direct contact, but not if they are separated by a layer of water.

Iron hydrogen bentonite was poured into the bottom of wide centrifuging tubes. Calcium bentonite gel held by adhesion in open glass tubes was placed above the iron hydrogen gel in a manner illustrated in figure 6. In system I the two gels remained separated by a layer of distilled water, 3 mm. in thickness. In system II the gels were in mutual contact. After 20 hr. it was found that ferrous ion had accumulated in the calcium bentonite of system II. In system I neither the gel nor the water layer developed the blue color of the ferrous ion test.

If a gel of iron hydrogen bentonite is separated from a hydrogen bentonite by a very thin collodion membrane, ferrous ion readily moves from one gel to the other. Collodion itself has no cation adsorption capacity, but the pores are sufficiently large so that the finer colloidal clay particles may be forced mechanically into the membrane. Contact between the two types of gel may thus be established. No transfer of ferrous ion is observed across thick collodion membranes. Although ferrous ion migrates from one gel to another through a very thin collodion membrane,

it will not pass through two thin membranes which are separated by a film of water (figure 7). This again is in harmony with the surface migration theory.

Surface migration of iron, and possibly manganese, has a number of interesting practical aspects, especially in regard to soil color and the formation of iron concentrations in soils and geological strata (e.g., laterites). The "nail experiment" suggests a simple explanation of the wide occurrence of spotted corrosion of iron pipes buried in acid soils.

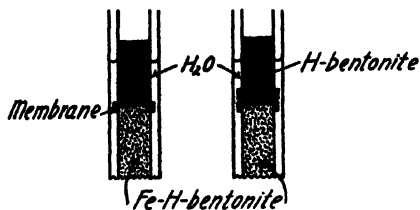


FIG. 7. Ferrous iron migrates from iron hydrogen bentonite into hydrogen bentonite through a thin collodion membrane but not through two membranes separated by a water film.

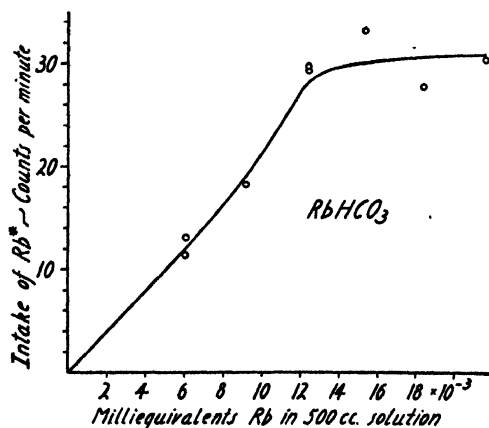


FIG. 8. Intake of radioactive rubidium by barley roots from solutions of rubidium bicarbonate.

Plant roots as colloidal systems

Plant roots possess many properties characteristic of colloidal systems. McGeorge (11) has found that roots as well as tops of numerous plants exhibit exchange adsorption. Mono- and di-valent cations replace each other in stoichiometric proportions. Barley roots studied by the authors have a cation adsorption capacity of 11 milliequivalents per 100 g. of oven-dry roots, as determined by the neutral ammonium acetate method. If living barley roots are immersed in rubidium bicarbonate solutions of

various concentrations for brief periods of time (1 sec., in order to avoid complications due to ion accumulation in the vacuoles), adsorption isotherms as shown in figure 8 are obtained. The rubidium bicarbonate solutions contained radioactive rubidium (Rb^*) and the intake was determined by measuring the radioactivity of the root. The volume of the solution was so large that the removed rubidium did not alter its concentration. We believe that the uptake of rubidium is a process of exchange adsorption. The maximum of the curve indicates that the outer portions of the root are saturated with rubidium. These colloid chemical relationships suggest that plant roots themselves exhibit the phenomenon of surface migration and contact exchange.

Contact intake and contact depletion

From the viewpoint of mineral nutrition of plants it appears expedient to divide contact exchange into contact intake and contact depletion

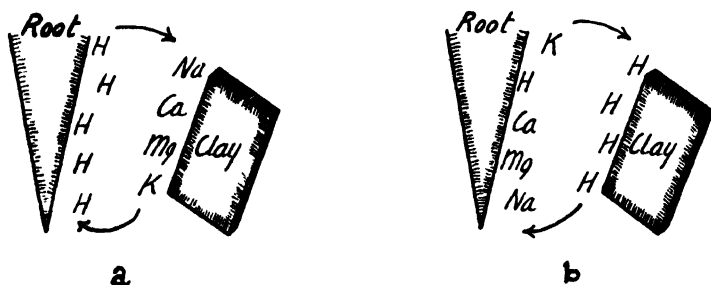


FIG. 9. Schematic representation of contact intake (a) and contact depletion (b) between plant roots and soil colloids.

(figure 9). In contact intake hydrogen ions on the root surface exchange for nutrient cations on the clay. The root system gains bases, whereas the clay particles become enriched in hydrogen ions. On the other hand, any nutrient ion on the root surface may be transferred to the clay surface. This is contact depletion, a process which involves disastrous consequences for the plant if the contacting colloid happens to be a hydrogen clay.

Experiments on contact depletion

Contact exchange studies require large amounts of uniform root material. Moreover, the roots must be healthy and in an active state of metabolism. Barley roots grown according to the technique of Hoagland and Broyer (7) fulfill these requirements. As a detailed account of contact depletion experiments has been published elsewhere (10), it may suffice to give but one or two illustrations. Excised barley roots were immersed for 10 hr.

in various electrolyte solutions and colloidal clay suspensions. Table 1 shows the reduction of the potassium content of the roots as a consequence of the various treatments. The effect of the electrolyte solutions is small and irregular. The clay particles, on the other hand, definitely lower the potassium level of the root; potassium migrates from the root surface onto the clay surfaces. The presence of a membrane, permeable to cations but not to clay particles, between root and soil colloids prevents the occurrence of contact depletion. The influence of the sign of the colloid furnishes further confirmation. If a root contains potassium cations and bromide anions, negative clay particles will pull out potassium but not bromide, whereas positive ferric hydroxide particles remove bromide but not potassium. Crucial experiments with radioactive elements indicate that the migration of nutrient elements from healthy

TABLE 1

Change in the total potassium content of barley roots as a result of contact exchange

TRUE SOLUTIONS		COLLOIDAL CLAY SOLUTIONS	
System	Change in per cent	System	Change in per cent
	<i>per cent</i>		<i>per cent</i>
NaCl.....	-4.1	Sodium clay ..	-13.7
NH ₄ HCO ₃	+1.6	Ammonium clay ..	-32.4
CaCl ₂	+1.4	Calcium clay ..	-5.8
HCl (pH = 4.1).....	-5.1	Hydrogen clay ..	-66.0

roots to clay particles appears to be a normal process of plant growth in soils.

Experiments on contact intake

The demonstration of accumulation of nutrient ions through contact intake involves a complicating factor, due to the presence of an unknown carbon dioxide gradient in the vicinity of the root. Carbonic acid may release the adsorbed ions on the clay particles by ordinary electrolyte exchange and the ions could then enter the root from the solution. In order to ascertain the presence of contact intake it must be shown that plants accumulate more ions from clay suspensions than from their carbonic acid extracts.

Hydrogen clays were treated with radioactive rubidium carbonate in various concentrations, followed by aeration to remove carbon dioxide. The resulting rubidium hydrogen clays had various degrees of saturation (9) with respect to rubidium. The degree of saturation (*D*) indicates the portion of the ions on the surface of the clay particles represented by rubidium. In other words, all rubidium hydrogen sols contained iden-

tical amounts of rubidium ion but varying amounts of hydrogen ion. Healthy barley roots (1 cork) were dipped into the suspensions for 1 sec. and the transfer of Rb^* from the clay to the root was determined with the aid of a Geiger counter. The curve shown in figure 10 depicts the relationship between rubidium intake and degree of saturation of the clay particles.

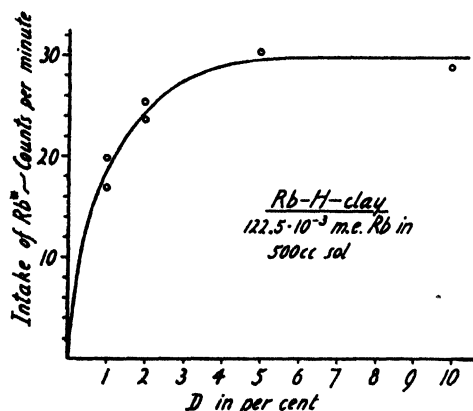


FIG. 10. Intake of radioactive rubidium by barley roots from rubidium hydrogen clay suspensions of various degrees of saturation (D) of clay particles.

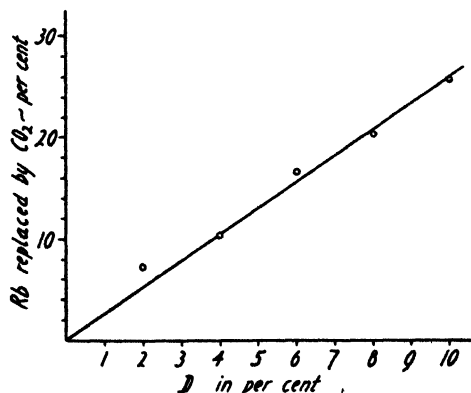


FIG. 11. Replacement of adsorbed rubidium by carbonic acid at various degrees of saturation (D) of clay particles.

At the same time aliquots of the original rubidium hydrogen clay suspensions were saturated with carbonic acid for 48 hr., centrifuged, and the intermicellar liquid analyzed for Rb^* . The carbon dioxide exchange curve thus obtained is shown in figure 11. As the degree of saturation is lowered, the replacement of rubidium by carbon dioxide is decreased. By combining figures 8, 10, and 11 it is possible to construct a relationship between rubidium intake from rubidium hydrogen clay suspensions and

from the corresponding carbon dioxide-saturated intermicellar liquids (table 2). At low degrees of saturation of rubidium hydrogen clay, the suspensions are superior to their carbonic acid extracts, indicating the operation of contact phenomena. At higher values of D the differences disappear because the surface of the root is saturated with rubidium.

TABLE 2

Intake of radioactive rubidium by barley roots from rubidium hydrogen clay sols of various degrees of saturation (D)

CONCENTRATION OF SOL	D	INTAKE OF Rb* (EXPRESSED AS COUNTS PER MINUTE)		INCREASE OF CLAY OVER CARBON DIOXIDE EXTRACT
		From clay suspension	From carbon dioxide extract	
<i>per cent</i>	<i>per cent</i>			<i>per cent</i>
4.94	1.0	18.5	6	208
2.47	2.0	24.5	12.5	96
1.65	3.0	27.5	20	38
0.99	5.0	30	30	0

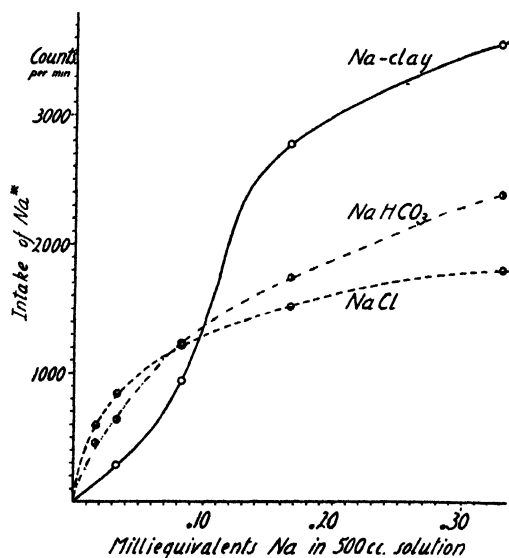


FIG. 12. Intake of radioactive sodium by barley roots from clay suspensions and salt solutions.

A very striking instance of contact relationships is observed with radioactive sodium. Roots of decapitated barley plants were immersed for 10 min. in various solutions of sodium clay ($D = 100$ per cent), sodium chloride, and sodium bicarbonate of equal concentrations of total sodium. The intake of radioactive sodium is shown in figure 12.

At higher sodium concentrations the accumulation of Na^+ from sodium clay greatly exceeds the intake from the corresponding solutions. It should be noted that the amount of sodium in the sodium bicarbonate solutions is equal to the total amount of sodium on the clay, and not merely to the carbon dioxide extract. The superiority of the clay system is beyond doubt. In other words, adding proper amounts of hydrogen clay to a solution of sodium bicarbonate stimulates the sodium accumulation of the roots.

At low sodium concentrations the situation is reversed. The clay curve is below the solution curves. This may be expected on theoretical grounds. In order that the roots may accumulate sodium, the ion must first strike the root surface. Now, for a small number of sodium ions, the probability that an ion hits the root surface is greater for solutions than for clay suspensions. In the latter systems the sodium ions are attached to but a few colloidal particles and the chances for contact are remote.

These experiments indicate that the entire science of mineral intake of plants in soils may be modified by this new approach, since the prevailing soil solution theories, dating back to the days of Liebig, are unable to account for the phenomena described. We believe that contact exchange and surface migration have widespread application in biology and agriculture.

SUMMARY

A theory of ionic movement in colloidal systems is proposed involving ions held in the adsorbed state on the surfaces of the micells.

The theory is used to interpret observations on the migration of ferrous iron in gels and sols of the bentonitic clays. The ions diffuse on the surface of the colloidal particles and "jump" from one particle to another. The theory suggests a new mode of mineral nutrition of plants in soils, based on interpenetrating double layers of root colloids and soil colloids. It is shown that roots in contact with clay particles gain as well as lose nutrient cations.

REFERENCES

- (1) BROOKS, S. C.: *Trans. Faraday Soc.* **33**, 1002-6 (1937).
- (2) CERNESCU, N. C.: *Anuar. inst. geol. României* **16**, 1-89 (1933).
- (3) COTTON, A., AND MOUTON, H.: *Les ultramicroscopes*. Masson et Cie, Paris (1906).
- (4) DUCLAUX, J.: *Colloid Chemistry* (edited by Jerome Alexander), Vol. I, pp. 515-24. The Chemical Catalog Co., Inc., New York (1926).
- (5) DUCLAUX, J.: *Diffusion dans les gels et les solides*. 50 pp. Paris (1936).
- (6) GIESEKING, J. E., AND JENNY, H.: *Soil Sci.* **42**, 273-80 (1936).
- (7) HOAGLAND, D. R., AND BROYER, T. C.: *Plant Physiol.* **11**, 471 (1936).
- (8) JENNY, H.: *J. Phys. Chem.* **40**, 501-17 (1936).

- (9) JENNY, H., AND AYERS, A. D.: Soil Sci., in press.
- (10) JENNY, H., AND OVERSTREET, R.: Soil Sci. 47, 257-72 (1939); 48, 9-24 (1939).
- (11) McGEORGE, W. T.: Plant Physiol. 7, 119-24 (1932).
- (12) SCHOFIELD, R. K.: Trans. Intern. Congr. Soil Sci., 3rd Congr., Oxford, 1935, Vol. I, pp. 30-3.
- (13) VANSELOW, A. P.: Soil Sci. 33, 95-113 (1932).
- (14) WINTERS, E.: Thesis, University of Illinois, 1938.

DIRECTLY AIR-DRIVEN TRANSPARENT ULTRACENTRIFUGES¹

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Different forms of the centrifuge and ultracentrifuge possess great value in the study of the composition and size of the particles. These comprise the batch-concentrating centrifuge of Wyckoff, the continuous-flow concentration process of Beams, the ultracentrifuge of Svedberg, the similar but much less expensive ultracentrifuge of Beams and Pickels, the powerful and versatile opaque ultracentrifuges of McBain, and even the simplest air-driven hollow rotor, or top, extensively used in France and Belgium. There is still, however, a place for directly air-driven transparent ultracentrifuges because (a) they are by far the least expensive, (b) they may be run at any desired constant temperature by first passing the driving air through a thermostat, (c) they may be adapted for use with very small quantities of material, and (d) starting and stopping require but a few seconds.

We here describe the directly air-driven transparent ultracentrifuge which is a development and refinement of the first air-driven one set up many years ago by McBain and O'Sullivan (6), and is now capable of measuring satisfactorily proteins as small as egg albumin. In addition we refer to the simplest form of transparent ultracentrifuge capable of taking a photographic record. This simple rotor has also served as a batch-concentrating centrifuge for our other transparent ultracentrifuge. The concentration and isolation of traces of substances for direct study is as important as is, in other cases, their complete elimination.

THE TRANSPARENT ULTRACENTRIFUGE WITH STATIONARY PERISCOPE

The essential improvements over the rotor of McBain and O'Sullivan (6) are: (a) the use of a spacing piece of platinum-iridium between the quartz windows of the cell to form a good heat-conducting non-deformable sectorial cell, short-circuiting any stray temperature gradients; (b) smoothing the interior of the rotor surrounding the periscope; (c) placing an enclosed air space above the cell; (d) insulating the cell from the rotor; (e) closing the opening of the cell with a small screw of stainless steel

¹ Presented at the Sixteenth Colloid Symposium, held at Stanford University, California, July 6-8, 1939.

covered with a film of beeswax; and (f) enlarging the guard around the stator to lessen the effects of turbulence in the confined air. Other minor details such as the use of the commercial type H-4 General Electric mercury vapor lamp, with outer glass jacket removed, may also be mentioned.

The information given by McBain and O'Sullivan (6) on the design of the stator, the effects of air pressure, etc., need not be repeated here.

At first we attempted to improve the temperature control by supplying air streams of suitable temperatures to the upper exposed surface immediately surrounding the periscope. However, this was abandoned in favor of the precautions listed above. It is helpful also to attach a sheet of Cellophane to the underside of the rotor above the periscope, although this sometimes tends to interfere with the photographic record. A metallic rotor is found to take the temperature of the escaping slip-stream of air, as measured by a copper-Constantan thermocouple placed 1 mm. from the edge of the rotor.

The guard is firmly mounted to avoid vibration. The stator rests upon blocks of sponge rubber, kept under slight compression by suitable tension of the rubber pressure tubing. It is used in an accurately level position.

Since a monochromator and monochromatic light are used, the line to be transmitted through the slit is picked out visually by making the first side of the slit fluorescent. It is useful to note that the 2804 Å line is that just below the absorption edge of "UV glass." The lens used was a Zeiss quartz anastigmat of focal length 12 cm., $f = 4.5$. With our small cell the much longer focal lengths commonly employed are unnecessary.

The angle of the stator is still 90° and that of the rotor cone 100°. Enlarging the latter angle to as much as 110° greatly increases the speed, but, owing to the greater Bernoulli effect, reduces the stability unless a stator with adjustable central air inlet is used. With the 7-cm. rotor to be described below, it was noticed that the ratio between the number of flutes cut on the rotor cone and the number of air ports in the stator should be an integer. The length of the flutes does not matter, but they must not reach the upper edge of the stator. The speed increases but little with increase in their number.

The length of the cell in a radial direction is 4 mm. and the diameter of the rotor is 37 mm.

THE COMPLETE TRANSPARENT ULTRACENTRIFUGE WITH BUILT-IN MIRRORS

The final design of our directly air-driven rotors is given in figure 1, which shows the way in which air friction at the cell windows is eliminated. There is an enclosed air space above the cell, made by screwing on a lid with two conical quartz windows cemented in place. All quartz is cut so as to be singly refracting.

albumin is 100. Thus the absolute magnitude of the cell is a matter of indifference, provided that facilities for accurate observation are available and the force is adjusted to yield the same resolving power.

SOME EXPERIMENTAL RESULTS

Hemoglobin

Some photographs are given for illustration in figure 2, and some microphotometer curves in figure 3.

Hemolyzed beef blood diluted with five parts of 1.2 *m* sodium chloride was used in five consecutive runs with the McBain-O'Sullivan rotor, photographs being made at 10-min. intervals. Each result was reduced to the sedimentation constant s_{20} , chosen by Svedberg as standard condition. The temperatures were 21.6, 21.9, 21.7, 22.2, and 21.8°C., respectively; relative viscosity = 1.15; density = 1.031; $G = 116,400$ g.

TABLE 1
Results with hemoglobin with O'Sullivan rotor

$s_{20} \times 10^{13}$	MEAN DEVIATION	MEAN
5.61, 4.75, 4.10, 3.82, 4.12, 4.83	0.60	4.54
5.47, 5.17, 4.55, 3.94, 4.24, 5.41	0.59	4.80
5.06, 5.04, 4.90, 4.79	0.12	4.95
5.12, 4.98, 4.10, 4.30	0.44	4.63
5.00, 4.27, 3.88, 3.80, 5.25	0.59	4.44
Mean.....		4.67
Standard deviation.....		0.18

One experiment with hemoglobin, performed with the rotor of the latest design but retaining the periscope, gave 4.51, 4.46, 5.11, and 4.11; mean, 4.69. A disk of Cellophane was fastened in the rotor above the periscope to improve the insulation of the cell. The microphotometer showed that the last two results were affected by an irregularity in the Cellophane which, if corrected, would bring them very close to the mean.

These results may be compared with the most accurate measurements of sedimentation constant yet reported for the oil turbine ultracentrifuge, given by Steinhardt (9):

$s_{20} \times 10^{13}$ 4.61, 4.68, 4.70, 4.54, 4.65, 4.61 \pm 0.05; mean, 4.63

These results superseded the previous Upsala value of 4.5, based upon unpublished data. They may be compared with the somewhat similar sedimentation constant for serum albumin obtained by von Mutzenbecher (7), using the Upsala ultracentrifuge: 4.20, 4.35, 4.2, 4.2, 4.34, 4.3, 4.1, 4.2, 4.23, 4.46, 4.30, 4.7, 4.6, 4.47, 4.5 \pm 0.20; mean, 4.45.

Egg albumin

A 1.36 per cent solution was prepared from crystalline egg albumin prepared by Dr. Eloise Jameson after dialyzing it until free from ammonium sulfate. Five consecutive runs at 1700 R.P.S. were made with the McBain-O'Sullivan rotor, showing that this had just reached its limit of fairly accurate measurement.

The mean values were 3.90, 3.05, 3.03, 2.35, and 2.57 (mean 2.98), instead of Svedberg's 3.55 and the value 3.56 obtained by McBain and Leyda (5) with their simple opaque analytical ultracentrifuge with the same egg albumin.

With the latest rotor, although still retaining the stationary periscope, five further runs with a new 1.08 per cent solution prepared by Dr. Eloise Jameson and running at over 1900 R.P.S. at various constant temperatures between 22° and 25°C., gave the following values: 3.66 (mean, 3.66); 3.57, 3.33, 3.67 (mean, 3.52); 3.96, 3.39 (mean, 3.67); 4.38, 3.30, 4.92 (mean, 4.20); 3.94, 4.10, 3.13 (mean, 3.72). The irregular values of the fourth experiment were again due to an irregularity in the Cellophane which was not corrected for. Omitting this, the final mean is 3.64 with standard deviation 0.08, as compared with Svedberg's already quoted 3.55. The result shows that the improved design of the rotor was completely successful.

An antibody fraction E_2 from rat blood serum

Interposed between the runs on egg albumin just quoted were measurements on a blood serum fraction separated electrophoretically by Dr. Eloise Jameson and containing an agglutinin, an antibody for sheep red blood cells. The total original solution, 0.3 cc., possessed a protein concentration of 0.1 per cent in 0.02 *m* phosphate buffer of pH 6.23, containing 0.15 *m* sodium chloride. This was evaporated to one-third its volume at 0.4°C. Only 0.003 cc. was required for each run. The first boundaries observed gave in two experiments the values: 3.50, 3.14, 3.54 (mean, 3.39); 3.18; the final mean was 3.34. This value resembles that of egg albumin, but the results are wholly different, the boundaries being perfectly sharp instead of diffuse, and on further centrifugation becoming stationary or even moving upwards again. Sharp boundaries due to gel formation have been noticed by Wyckoff (12), using activated bacteriophage. Gratia (3) centrifuged agglutinin for sheep red cells for 1 hr. in the Henriot and Huguenard centrifuge and obtained at that time no sedimentation, in contrast with other antibodies but in conformity with our results for that length of time.

Myosin

This muscle globulin consists of highly elongated particles showing stream double refraction with particle weight of about one million by the osmotic pressure method (11). A sample from dog prepared by C.C. Nimmo in 1.2 *N* potassium chloride of pH 7.6 sedimented at first with two sharp boundaries of which the lower was predominant. After a few hours, successive measurements gave a single sharp, not diffuse, boundary with mean values for $s_{20} \times 10^{13}$ equal to 14.7, 11.6, 11.4, and 10.5, successively, this behavior paralleling that known for denaturation.

THE SIMPLEST TRANSPARENT ULTRACENTRIFUGE

This new directly air-driven type has been announced (4) and will be described elsewhere. It consists of a solid metal cone carrying a slitted block of hard rubber supporting an ordinary capillary tube and recording on a piece of photographic film without the use of a camera or other accessories, and yet yielding accurate results for such proteins as that from the blood of *lumbricus* (59.6×10^{-13}) and hemoglobin (4.71×10^{-13}).

SUMMARY

1. The present definitive development of the direct air-driven transparent ultracentrifuge is described. It gives results equal in accuracy to those of any other transparent ultracentrifuge down to proteins as small as egg albumin.

2. It is emphasized that, in accordance with the classical mathematical analysis of Mason and Weaver, all monodisperse substances give an identical distribution in any ultracentrifuge provided that the resolving power, $1/\alpha$, is kept constant. Since this is proportional to the field of force, the particle weight, and the radial length of cell, there is no theoretical difference whatsoever between cells of different dimensions so long as this product is maintained constant.

REFERENCES

- (1) ARCHIBALD, W. J.: *Phys. Rev.* **54**, 371
- (2) BAUER, H.: *Biochem. Z.* **100**, 52 (1919).
- (3) GRATIA, A., AND GORECZKY, L.: *Compt. rend. soc. biol.* **126**, 900 (1937).
- (4) McBAIN, J. W., AND LEWIS, A. H.: *Science* **89**, 611 (1939).
- (5) McBAIN, J. W., AND LEYDA, F. A.: *J. Am. Chem. Soc.* **60**, 2998 (1938).
- (6) McBAIN, J. W., AND O'SULLIVAN, C.: *J. Am. Chem. Soc.* **57**, 780, 2631 (1935).
- (7) MASON, M., AND WEAVER, W.: *Phys. Rev.* **23**, 412 (1924).
- (8) VON MUTZENBECHER, P.: *Biochem. Z.* **266**, 250 (1933).
- (9) STEINHARDT, J.: *J. Biol. Chem.* **123**, 543 (1938).
- (10) SVEDBERG, T.: *Z. physik. Chem.* **127**, 51 (1927).
- (11) WEBER, H. H., AND STÖVER, R.: *Biochem. Z.* **259**, 289 (1933).
- (12) WYCKOFF, R. W. G.: *Cold Spring Harbor Symposia Quant. Biol.* **6**, 361 (1938).

THE ACTION OF RADON ON POLYMETHYLENES: CYCLOBUTANE AND CYCLOBUTENE

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The polymerization of cyclopropane, cyclopentene, and cyclopentane by α -particles from radon has been reported (5). The polymerization of cyclobutane and cyclobutene by treating with radon has been carried out to complete the information for the first five members of the series of saturated polymethylenes and to increase the data available for the unsaturated series. The bombardment of cyclobutane by α -particles is of especial interest on account of the anomalous behavior of the hydrocarbon. For example, the ring is opened on hydrogenation at temperatures only somewhat over 100°C. or on bromination. Then, too, the ring breaks rather readily at two places, resulting in the formation of two molecules of ethylene or its derivatives (10). This behavior has been attributed to the presence of strains in the four-carbon atom ring. Baeyer (1) and others have pointed out that the valence angles of the carbon atom are distorted $9^{\circ}44'$ in tetramethylene.

The greater reactivity of cyclobutane suggests a larger value of the $-M/N$ ratio than would be normally expected. On the other hand, the positive heat of formation (16.8 calories) from the diamond and molecular hydrogen, calculated by the method of Kharasch (7), suggests that the value for the $-M/N$ ratio will be small,—about 2 (4). The negative heat of formation of cyclobutene (-6.0 calories), as well as its unsaturated nature, lead to the prediction of a value for $-M/N$ greater than 2.

The summarized data for the action of radon on the polymethylenes are given in table 1. The value for ethylene (9) is included, since this gas may be regarded as the simplest member of the polymethylene series. It should be noted that cyclobutene, which has a negative heat of formation, has a value for $-M/N$ of 7.4, while the value of $-M/N$ for cyclobutane, whose heat of formation is positive, is 2.2. The values then agree with the relationship previously pointed out (4). The existing data are given in figure 1.

With the exception of ethylene the value of the ratio $\Delta(H_2 + CH_4)/-\Delta HC$ decreases consistently with the increase in the ratio $-M/N$.

TABLE 1
Action of radon on polymethylenes

HYDROCARBON	HEAT OF FORMATION FROM THE DIAMOND AND HYDROGEN	$-M/N$	$\frac{+\Delta(H_2+CH_4)}{-\Delta HC} \times 100$
Cyclopropane.....	-15.3	3.3	20.5
Cyclobutane.....	16.8	2.3	33.4
Cyclopentane.....	18.9	1.7	73.7
Ethylene.....	-6.4	4.8	16.0
Cyclobutene.....	-6.0	7.4	5.8
Cyclopentene.....	-1.8	4.5	19.2

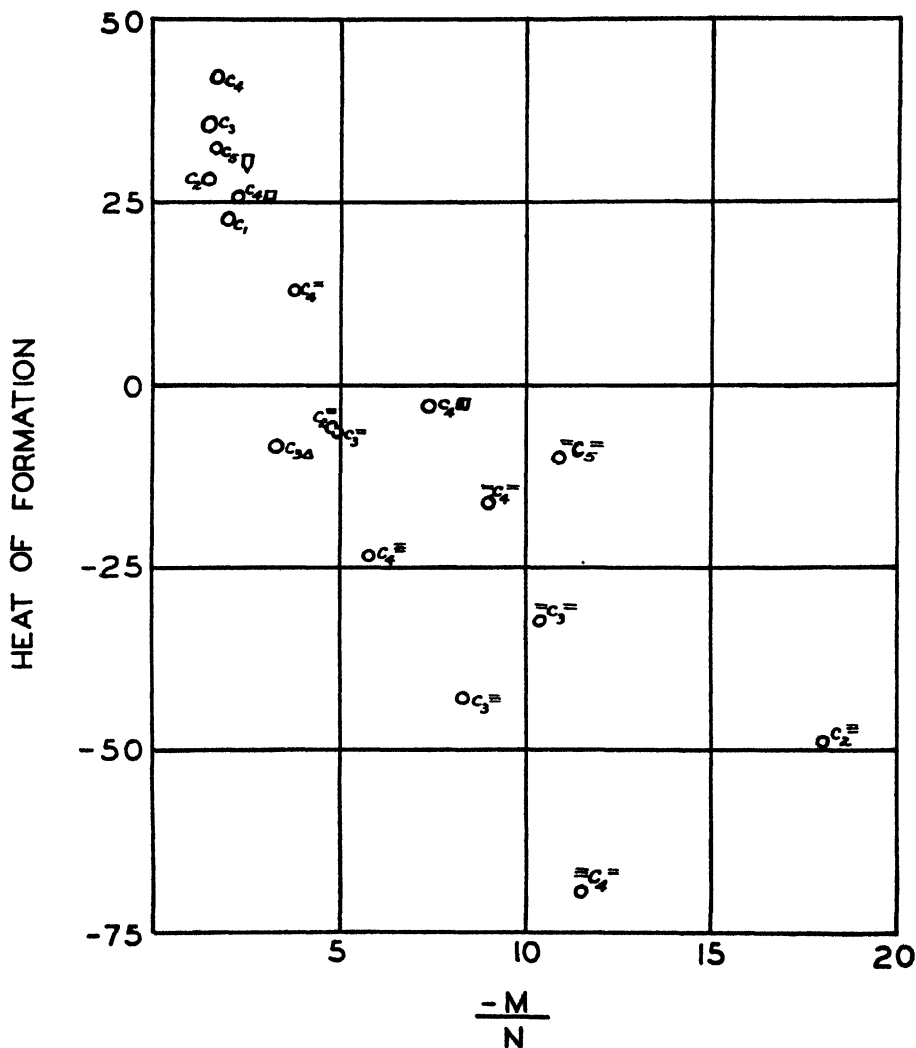


FIG. 1. Plot of heat of formation against values of $-M/N$ for the polymethylenes

The available data are given in figure 2. Cyclobutene and cyclobutane act in a normal manner in this respect when bombarded with α -particles.

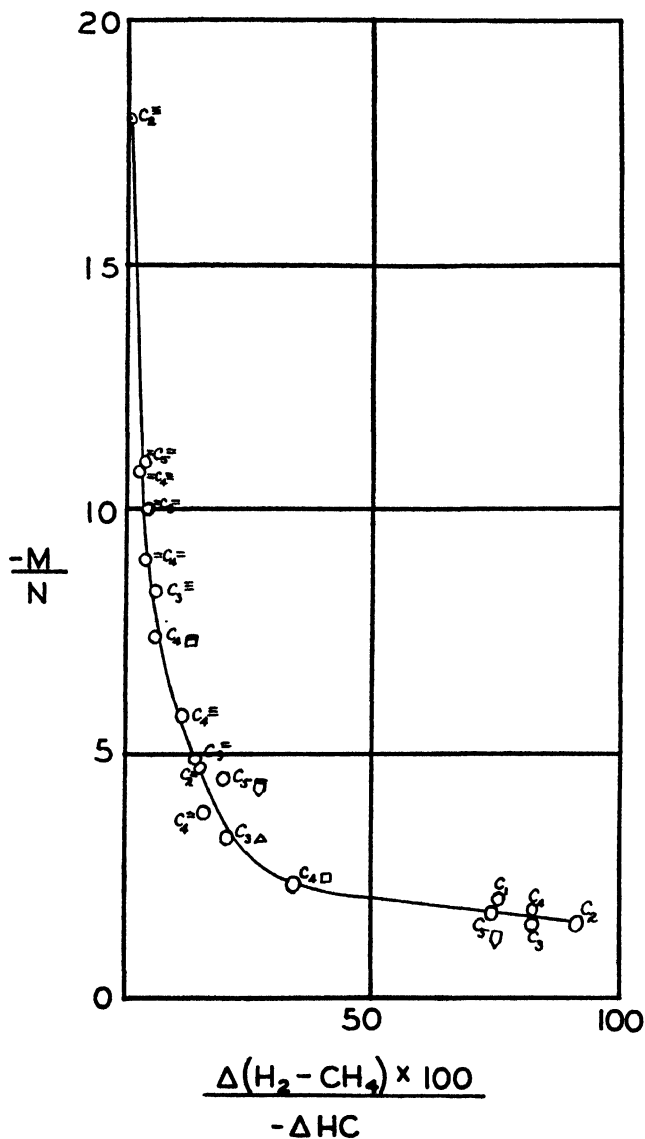


FIG. 2. Plot of the ratio $\Delta(\text{H}_2 + \text{CH}_4) \times 100 / -\Delta \text{HC}$ against values of $-M/N$ for the polymethylenes

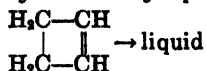
PREPARATION OF CYCLOBUTENE AND CYCLOBUTANE

All attempts to prepare these hydrocarbons were unsuccessful until 1907 when Willstätter and Bruce (11) announced a synthesis

which involved ten steps with an overall yield of about 10 per cent.¹

By going from cyclobutanecarboxylic acid directly to cyclobutylamine, the preparation of the acid chloride and the acid amide, and the Hofmann rearrangement of the acid amide to the amine have been eliminated. The

TABLE 2
Polymerization of cyclobutene by alpha rays from radon



Temperature, 25°C.; $s = 2.42$; $i = 1.28$; $is = 3.09$. Reaction sphere: volume = 32.05 cc.; diameter = 3.94 cm.; $E_0 = 0.01598$ Curie

TIME		RADON	PRESSURE			$\frac{\Delta(\text{H} + \text{CH}_4)}{-\Delta\text{HC}} \times 100$	$(k\mu/\lambda)'$	$\frac{-M_{\text{C}_4\text{H}_6}}{N_{\text{C}_4\text{H}_6}}$
Days	Hours		Total	C_4H_6	$\text{H}_2 + \text{CH}_4$			
		per cent	mm.	mm.	mm.			
		100.000	531.6	531.6	0	0		
	1.47	98.904	526.6	526.6	0	0	53.9	7.2
	5.37	96.053	514.6	514.6	0	0	50.5	6.8
	9.65	93.019	501.0	500.3	0.7	4.9	58.4	7.8
	14.02	90.019	489.1	487.4	1.7	7.8	54.3	7.3
1	0.83	83.009	461.1	458.7	2.4	2.4	54.3	7.4
1	5.00	81.520	451.8	447.9	3.4	9.3	51.9	7.2
1	10.33	77.299	440.9	436.9	4.0	5.5	54.5	7.6
2	1.72	68.878	413.1	407.4	5.7	5.8	52.0	7.3
2	6.38	66.509	405.8	399.6	6.2	6.4	51.1	7.4
2	13.67	62.939	394.8	387.7	7.1	7.6	52.9	7.6
3	2.52	57.186	378.1	370.3	7.8	4.0	49.9	7.3
3	9.11	54.471	371.0	362.9	8.1	4.1	46.7	6.9
4	1.33	48.224	354.7	345.3	9.4	7.4	49.8	7.4
4	8.78	45.574	348.6	338.8	9.8	6.2	45.1	6.8
5	0.92	40.381	335.7	325.6	10.1	2.3	47.7	7.2
5	9.78	37.785	330.0	319.2	10.8	11.0	47.7	7.2
6	7.97	31.989	316.1	304.3	11.8	6.7	52.3	8.0
7	3.63	27.605	306.6	294.3	12.3	5.0	47.7	7.4
9	4.35	19.153	289.5	276.7	12.8	2.8	45.7	7.1
21	1.58	2.024	258.1	243.3	14.8	6.0	47.1	7.5
Weighted average						5.8		7.4

last step was particularly bad, since the yield was only 22 per cent. The elimination of these steps has resulted in an overall yield of 29.4 per cent. The vapor pressures of the hydrocarbons have been determined. The details of the preparation and the vapor pressure data will be published elsewhere.

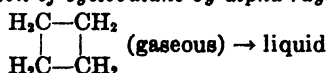
¹ This yield is a composite one, since no one author gives the yields for each step.

ACTION OF α -PARTICLES ON THE HYDROCARBONS

The gases were mixed separately with radon in the apparatus previously used. Shortly after the gases were mixed with the radon, a fog formed. Within a few hours droplets of a clear colorless liquid were deposited,

TABLE 3

Polymerization of cyclobutane by alpha rays from radon



Temperature, 25°C.; $s = 2.78$; $i = 1.28$; $is = 3.56$. Reaction sphere: volume 39.45 cc.; diameter = 4.22 cm.; $E_0 = 0.04571$ Curie

TIME		RADON	PRESSURE			$\frac{\Delta(\text{H}+\text{CH}_4)}{-\Delta\text{HC}} \times 100$	$(k\mu/\lambda)'$	$\frac{-M\text{C}_4\text{H}_8}{N\text{C}_4\text{H}_8}$
Days	Hours		Total	C_4H_8	(H_2+CH_4)			
		per cent	mm.	mm.	mm.			
		100.000	589.1	589.1	0.0			
	3.02	97.760	585.7	581.0	4.7	58.1	135.0	1.91
	6.40	95.314	577.8	571.1	6.7	20.2	154.5	2.19
	9.65	93.018	570.8	561.4	9.4	28.9	162.4	2.30
	13.37	90.459	562.9	551.4	11.5	21.1	153.5	2.18
	23.42	83.892	542.9	524.4	18.5	26.0	167.2	2.37
1	2.80	81.791	536.9	516.0	20.9	28.6	167.9	2.38
1	5.57	80.110	532.6	510.4	22.2	23.2	143.9	2.05
1	8.15	78.575	528.4	504.8	23.6	25.0	157.5	2.24
1	13.92	75.246	519.5	491.9	27.6	31.0	169.5	2.43
1	23.62	69.968	507.1	473.4	33.7	33.0	159.4	2.30
2	3.47	67.976	502.3	466.9	35.4	26.2	151.8	2.21
2	7.90	65.756	497.7	460.6	37.1	27.0	133.9	1.96
2	14.25	62.696	491.6	450.5	41.1	39.6	158.1	2.33
3	1.28	57.722	480.9	434.7	46.2	32.3	157.0	2.33
3	8.87	54.526	474.7	424.8	49.9	37.4	157.6	2.37
3	23.15	48.990	464.6	409.3	55.3	34.9	147.5	2.25
4	8.22	45.767	458.6	401.0	57.6	27.7	139.2	2.16
4	23.30	40.874	450.5	387.8	62.7	38.6	149.3	2.35
5	23.27	34.149	440.4	371.4	69.0	38.5	140.8	2.26
6	8.73	31.810	437.0	365.2	71.8	45.2	157.2	2.56
8	8.42	22.244	424.2	344.0	80.2	39.7	136.4	2.29
11	8.17	12.989	413.4	325.4	88.0	42.0	131.7	2.31
14	0.00	8.046	406.5	314.8	91.7	35.0	146.8	2.66
Weighted average						33.4		2.28

especially on the lower hemisphere of the container. The viscosity of the products increased with the time of the action. The data are given in tables 2 and 3.

The data have been interpreted according to the ion cluster theory of Lind (8), and the calculations have been made as described in previous

papers (3). That other interpretations are possible seems likely, since recently Eyring, Hirschfelder, and Taylor (2) developed a theory to account for the radiochemical synthesis of hydrogen bromide, involving known processes of ionization, excitation, and neutralization of the ions to account quantitatively for the data. Hirschfelder and Taylor (6) have extended the theory to the corresponding reactions in carbon monoxide, oxygen, and carbon dioxide.

SUMMARY

The synthesis of cyclobutane and of cyclobutene has been simplified, thereby increasing the yield threefold.

These gases polymerize to liquids whose viscosity and color increase with the time of bombardment by α -particles from radon. The $-M/N$ value of cyclobutane with a heat of formation of 16.8 calories is 2.3, and that of cyclobutene, having a heat of formation of -6.0 calories, is 7.4. These values agree with the relationship previously noted. The values of the ratio $\Delta(\text{H}_2 + \text{CH}_4)/-\Delta\text{HC}$ decrease consistently with the increase in the $-M/N$ value.

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REFERENCES

- (1) BAEYER: Ber. **18**, 2277 (1885).
- (2) EYRING, HIRSCHFELDER, AND TAYLOR: J. Chem. Phys. **4**, 479, 570 (1937).
- (3) HEISIG: J. Am. Chem. Soc. **53**, 3245-63 (1931).
- (4) HEISIG: J. Phys. Chem. **36**, 1000-5 (1932).
- (5) HEISIG: J. Am. Chem. Soc. **54**, 2328-32 (1933); J. Phys. Chem. **39**, 1067-73 (1935).
- (6) HIRSCHFELDER AND TAYLOR: J. Chem. Phys. **6**, 783 (1938).
- (7) KHARASCH: J. Research Natl. Bur. Standards **2**, 374 (1929).
- (8) LIND: The Chemical Effects of Alpha Particles and Electrons, American Chemical Society Monograph, p. 163. The Chemical Catalog Co., Inc., New York (1928).
- (9) LIND, BARDWELL, AND PERRY: J. Am. Chem. Soc. **48**, 1558-75 (1926).
- (10) PERKIN AND COLMAN: J. Chem. Soc. **51**, 228 (1887).
- (11) WILLSTÄTTER AND BRUCE: Ber. **40**, 3979 (1907).

THE PHASE RULE BEHAVIOR OF CONCENTRATED AQUEOUS SYSTEMS OF A TYPICAL COLLOIDAL ELECTROLYTE: SODIUM OLEATE¹

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This paper is in the nature of a preliminary report on the phase rule behavior of sodium oleate and water, there being no previous study in the literature. The purpose of this investigation was to determine whether the sequence of phases intermediate between crystalline curd fiber phase and isotropic liquid, recently discovered (17, 18) in the case of anhydrous sodium palmitate also exists for sodium oleate, and, if so, to determine the relation between them and the phases existing in aqueous soap systems. The results obtained further serve to show once more that colloidal phases can participate in reversible equilibria exactly as described by the phase rule of J. Willard Gibbs.

The present work gives a provisional model of the phase rule diagram, although much still needs to be done before some of the phase boundaries in the more concentrated systems can be regarded as finally established. Anhydrous sodium oleate appears to have five separate stable phases between 20°C. and its melting point at 241°C. Anhydrous sodium palmitate had five between its genotypic point (62°C.) and its melting point (292°C.). M. J. Vold has now demonstrated the existence of an additional transition in anhydrous sodium palmitate at about 172°C. The new phase has been named "superwaxy soap." Each of these phases can dissolve some water before disintegrating, so the phase rule diagram shows a series of separate areas corresponding to the extension of these phases into the aqueous system. In addition, there are possibly three liquid crystalline solution phases, which exist only in the aqueous system and have no counterpart in the anhydrous soap. One of these, middle soap, has been familiar since its original discovery by McBain (5, 10).

EXPERIMENTAL METHODS

Materials

Oleic acid, prepared by the Lapworth method, was obtained from the British Drug Houses, Ltd. It had an iodine number of 87.1. Sodium

¹ Presented at the Sixteenth Colloid Symposium, held at Stanford University, California, July 6-8, 1939. Revised in proof.

oleate was prepared from this acid by neutralization (phenolphthalein as indicator) of a hot alcoholic solution with an alcoholic solution of sodium ethylate. Analysis of the dried product by standard methods gave the following results: real soap, 99.3 per cent; water, 0.5 per cent; free sodium hydroxide, 0.006 per cent. Allowance was made for the water in making up samples. The iodine number of the oleic acid recovered from this soap by acidification and ether extraction was only 81.2, while its molecular weight was 284.1. Preparation in an atmosphere of nitrogen did not prevent this decrease in the iodine number. The impurity introduced may not affect the phase behavior seriously, as is shown by the fact that the anhydrous material melted fairly sharply, over a 2–3°C. range, and by the fact that in the composition range between 0 and 25 per cent sodium oleate, where other results are available for comparison (4, 15), the solubility curve for curd fiber phase agrees within a maximum deviation of 3° with that determined using independent samples of sodium oleate.

The synthetic method

This method consists of visual observation of the temperatures of phase change when a sample of known composition is heated or cooled. Determination of the temperature (T_i), at which a liquid crystalline phase first appears when isotropic liquid is cooled has already been described (7). Essentially the same procedure was followed in the present work. Temperatures were read on a thermometer calibrated under conditions of use by direct comparison with a series of standardized Anschütz thermometers and provided with a metal lag to make it follow the changing temperature of the soap sample more closely. The observation chamber was a small well-stirred air oven provided with glass windows. Crossed Polaroids were occasionally used to facilitate detection of the first traces of anisotropic material. Individual values of T_i are probably precise within 2°C., except where middle soap is the saturation phase, where the uncertainty may be 5°C.

Careful observation of the contents of the tube by transmitted light during slow cooling reveals several changes in addition to " T_i ." Correlation of these changes with actual phase transitions is not always possible, since, while the appearance may be very different at two temperatures, the determination of a unique temperature at which the alteration began or became complete is frequently impossible. The changes in appearance consist of diminished translucence, sudden increase in the number of bubbles in the sample, appearance of a milky opacity in the translucent liquid crystalline material, complete loss of opacity, etc. In samples containing from 56 to 85 per cent sodium oleate the apparent viscosity, judged by the ease with which the systems may flow under their own weight, goes through a pronounced minimum as the temperature is lowered, first increasing, then decreasing markedly, and finally increasing again.

The determination of " T_c " as the temperature at which the last trace of curd fiber phase disappears on heating has also been previously described (7). This observation consists in attempting to determine visually the temperature at which the last trace of opaque "solid" disappears to form isotropic liquid or transparent jelly or translucent anisotropic liquid. It now seems certain that the actual observations in more concentrated systems (>45 per cent soap) may refer to disappearance of the aqueous counterparts of subwaxy or waxy soap, rather than only to transformation from stark white curd to the duller waxy form, and in some regions their significance is not yet clear (see table 1). In systems where isotropic liquid or jelly or middle soap are formed on heating, the transformation recorded as T_c is very sharp and its determination is precise within 1.5°C. That crystalline curd fibers are here the saturating phase is also indicated by the extensive undercooling that can be observed. In more concentrated systems, where the change is much more difficult to detect, undercooling does not seem to occur to an appreciable extent, the temperature obtained on cooling an 85.2 per cent system agreeing within 3°C. with that obtained on heating, thus supporting the hypothesis that one of the waxy phases is formed here on cooling, rather than crystalline curd fiber phase.

Dilatometric studies

The curve of specific volume *versus* temperature for anhydrous sodium oleate was determined in this laboratory by Mr. M. Macomber, using the technique described by Vold and Vold (18).

The method has been extended to aqueous systems by M. J. Vold and will be described in detail in a subsequent communication. In brief, samples previously homogenized by heating to isotropy are introduced into the bulb of a dilatometer, the remainder of the bulb and the lower portion of the capillary are filled with mercury, and the top of the capillary is sealed. The observed increase of volume with increasing temperature is a composite of thermal expansion, phase changes in the soap, and formation of steam. At high temperatures the latter is the dominant effect. Moreover, once a sample has been heated to about 120°C., the formation of vacuoles on cooling and occasional partial segregation of phases frequently vitiate subsequent results. The volume change accompanying complete transformation of one phase to another most usually occurs over a range of temperature in two-component systems, with the result that the "flats" readily detected with anhydrous soaps are replaced by curves of changed slope, more difficult to determine. Consequently the temperatures of phase change reported on the basis of this dilatometric work in aqueous systems must be regarded as provisional and can be accepted only where they are self-consistent and in accord with other data. Despite these reservations, however, the dilatometric investigation has yielded

TABLE 1*
Visual observations

SODIUM OLEATE	T_i	" T_c "	DEVELOPMENT OF BUBBLES AND PARTIAL LOSS OF TRANSLUCENCY	DEVELOPMENT OF GREATER OPACITY	OTHER CHANGES
weight per cent	°C.	°C.	°C.	°C.	°C.
1.53		20.1			
3.55		24.2			
5.05		23.6			
9.87		24.1			
14.9		24.9			
17.4		25.6			
20.2		26.6			
20.9		27.2			
22.5		27.4			
24.0		27.8			
25.0		28.5			
27.4	58	31.6			
30.0	80	32.6			
32.5	92	32.4			
35.1	117	33.1			
37.5	127	32.8			
40.0	133	34.0			
42.7	123	33.5 (36.0)			
45.0	102	33 (35.7)			
46.2	127	33			
47.5	152	32 (41.2)			
50.5	177	33 (48.4)			
52.9	197	33.5 (56.7)			80
55.3	215	33 (64.2)			
60.6	239	34 (70.3)			
65.3	247	36 (75.6)	180		
68.5	252	42.5 (77.5)	210		120
73.5	256	49 (80.7)	230	132	
74.3	255.5	(80.1)	189	130	
75.0		(78.7)		143	
77.5	255	65 (79.0)	205	101	

* Up to 73.5 per cent sodium oleate the " T_c " values given in table 1 probably refer to the disappearance of curd fiber phase. In more concentrated systems the values reported as " T_c " probably refer to the disappearance of subwaxy or waxy soap. Systems containing 74.3 per cent or more of sodium oleate all appeared to change from glassy white to dull cream color at a temperature near 48°C. or slightly lower.

TABLE 1—*Concluded*

SODIUM OLEATE	T_i	" T_g "	DEVELOPMENT OF BUBBLES AND PARTIAL LOSS OF TRANSLUCENCY	DEVELOPMENT OF GREATER OPACITY	OTHER CHANGES
<i>weight per cent</i>	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$
80.8	253	77 (81.0)	173		222
85.0	251	99.2	205		222
85.2	251	98 (97.0)	166		
88.3	243	113	204		
91.0	239	127	215		
93.4	234	142			
95.0	235	165		85	
96.4	200				
97.3	230	190		101	
98.3	233	199		92	
99.5	241	196		106	

TABLE 2

Data obtained by the dilatometric method

SODIUM OLEATE	TEMPERATURES OF INFLECTIONS IN VOLUME-TEMPERATURE CURVES
<i>weight per cent</i>	$^{\circ}\text{C.}$
54.0	37; 64; 73; 89; (69)*
58.8	32; 68; 88
69.3	32; 45; 78; 90
72.8	39; 51; 70; 78; 94
79.3	36; 72; (61)
80.6	41; 65; 70; 92
89.0	78; 103-108; (56; 155; 166; 183)
91.5	47; 69; 108; (61; 85; 98)
94.7	37; 60; 80; 98; 224; 237
96.7	47; 199
100	68; 122; 179; 201

* Values inclosed in parentheses are less certain than the others listed for the same sample.

significant information, especially at temperatures below 110°C. with systems containing more than 50 per cent soap, where most other methods used are not applicable.

The results of these dilatometric studies are contained in table 2.

Vapor pressure determinations

The utilization of isothermal vapor pressure-composition curves for the determination of the phase behavior of soap systems has already been

discussed (16). The sorption balance devised by McBain and Bakr (6) has been adapted to measurement of vapor pressures by an isopiestic method. A 16-mg. sample of soap is hung in a small platinum bucket at the end of a calibrated fused silica spring in the upper portion of a sealed evacuated tube whose lower portion contains water. The composition of the sample at a fixed temperature is determined as a function of the vapor pressure, maintained at any desired value by a thermostat surrounding the lower portion of the tube, by observing the extension of the spring with a travelling microscope. The author is indebted to Dr. J. L. Porter for assembly of the apparatus, the details of which will be given in papers shortly to be communicated by McBain, Vold, Porter, and Vold.

Measurements have been made in duplicate at 101.5°C. of the vapor pressure of water above samples of sodium oleate containing from 0 to 35 per cent water. While the behavior in systems containing less than 7 per cent water is still not thoroughly understood, undercooling or lack of reversibility being the probable origin of the effects observed, the curves yield one result of phase rule significance. The vapor pressure appears to be independent of composition between 89.9 and 84.8 per cent sodium oleate, showing that two condensed phases coexist in this range. The two samples were in agreement as to the compositions at the extremities of the flat within 1.5 per cent.

Microscopic observations

Microscopic observations using crossed Nicols were made with systems of given composition both on heating and on cooling in order to supplement the results obtained by the synthetic method. The microscope, hot stage, and method of temperature measurement were the same as those already described (18). Samples were prepared by transferring a small lump of soap of the desired composition from a reservoir tube to a small flattened glass capillary, which was then sealed. Uniformity was ensured by prior homogenization of the reservoir sample at temperatures above its melting point to isotropic liquid. The finished microscope cells were about 17 mm. long, 2 mm. wide, and 0.2 to 0.6 mm. thick, internally. Prior to microscopic examination, each cell was heated well above its T_i , so that the soap might run together to form a coherent mass. Considerable change in composition can occur during preparation of a sample in this manner. The final composition of each sample was determined from the microscopically observed T_i by reference to the previously determined T_i -composition curve. The validity of this procedure was checked by comparing microscopic T_i values with the macroscopic curve for a few samples prepared by weighing the soap and water directly into the cell on a semi-micro balance.

The principal experimental difficulty encountered is the tendency for

inhomogeneity of composition to develop, owing to distillation of water from hotter to cooler portions of the cell. This difficulty was minimized by making the cells as short as possible, by supporting the cell out of contact with the walls of the hot stage on a glass slide, etc. In general, T_i was determined both at the beginning and at the end of a series of microscopic observations, and results on samples which were found to have fractionated were discarded. Nevertheless, it seems likely that some undetected fractionation may have occurred and been responsible for some of the erratic results obtained.

In general, a magnification of about 175 diameters was used. With such thick samples (0.2 to 0.6 mm.) the whole field of view is not all in focus simultaneously, and characteristic optical figures may be difficult to recognize. However, concealment of genuine phase changes by spurious maintenance of the physical form of a phase oriented at a glass surface to temperatures considerably higher than the true transition temperature is minimized by this procedure.

All the results of microscopic observations are summarized in table 3. The values of T_i are the average of four or more determinations made on both heating and cooling and usually agreeing within 2°C.

T_0 is the temperature at which isotropic liquid first appears on heating. The contrast between dark isotropic liquid and bright liquid crystal between crossed Nicols is so great that this observation can be made as precise as T_i determinations. In a composition range near 60 per cent sodium oleate, isotropic liquid and liquid crystal are present together in two separate temperature ranges. In these systems it is possible to observe not only the temperature of first formation of isotropic liquid but also temperatures of sudden increase or decrease in the proportion of isotropic liquid.

Some phase changes not involving isotropic liquid can also be recognized by the accompanying characteristic change in appearance. One of these is the change from a dull stippled structure to the coarse bright golden structure characteristic of phase B (compare, for example, figures 15 and 6). Other such changes are those marked by a pronounced increase in brightness of the field of view, as recorded in columns 4, 5, and 6 of table 3.

Frequently observations at fairly well separated temperatures show that the structure of a sample has changed, but the temperature at which the change occurs can not be closely determined because of the gradual replacement of the one structure by the other. Figures 4 and 5 show the characteristic appearance associated with phase A, figure 6 is illustrative of phase B, figure 7 of phase B probably mixed with some isotropic liquid, and figure 8 of middle soap (at low temperatures).

Sometimes there is no significant change in appearance at a composition and temperature where a phase change is definitely known to occur on the

TABLE 3

Apparent transition temperatures obtained by microscopic observations

T_i	SODIUM OLEATE	T_o	TEMPERATURES AT WHICH CHANGES 4 TO 13 OCCUR									
			4	5	6	7	8	9	10	11	12	13
$^{\circ}\text{C.}$	weight per cent	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$
127*	36.3	106	—	—	—	—	—	—	—	82	—	—
95*	43.8	70	—	—	—	—	—	—	—	—	85	—
168	49.1	69?	?	41	62?	—	106	—	—	—	128?	—
	52.8	81	—	—	52	—	—	73?	—	{63 78}	—	—
224	57.2	72?	—	48	—	—	—	—	80?	—	{126 153 203}?	{144 167}?
230	58.8	{59? 70}	?	34	—	—	—	—	185	208	162	131
243	63.3	236	40	68	—	—	—	{113 ↑ 129 ↓}	129	200	—	—
249	67.0	240	40	57	—	—	—	{115 ↑ 102 ↓}	{115 ↑ 102 ↓}	150	—	—
254	71.3	248	37	46?	104	—	—	181	{144 ↑ 163 ↓}	—	—	—
242	89.0	235	77?	—	89?	—	—	108?	108?	186	—	—
240	90.3	230	38	58	47	—	—	?	—	{107 203}	—	—
238*	91.5	225	—	93?	115	186	—	136?	—	215	—	—
236	92.0	224	?	58?	—	—	143?	99	—	123	—	—
231*	94.4	226	?	62	103	159	122	207	{179 ↑ 192 ↓}	—	—	—
234	95.0	218	42	63	77	—	187	93	—	126?	—	—
213*	96.5	202	49	64	100	158	181	—	—	196	—	—
242*	99.5	—	65	—	109	207	220	—	—	—	—	—

The changes occurring at the temperatures designated may be briefly summarized as follows: 4, change from featureless curd to the first visible structure; 5, increase in brightness, color change from dull yellow to whiter yellow, more pronounced structure visible; 6, marked increase in brightness, slightly coarser structure, all dull patches gone, much whiter golden color; 7, some softening, some development of polarization colors, development of a medium coarse structure; 8, great increase in brightness and in the variety of polarization colors, appearance of somewhat larger rounded structures; 9, formation of a very coarse structure of rounded velvety areas, very bright golden color; 10, formation or disappearance of "palisade structure" (figure 10); 11, uncertain changes of questionable reality; 12, faster rate of melting or reformation of isotropic liquid on further heating; 13, increase in amount or reformation of liquid crystal on further heating.

Values of T_i marked with an asterisk were determined on samples whose composition was independently known by weight. Dashed spaces in the table mean that the transition in question was not observed. Blanks in the table mean that the sample was not adequately studied over that temperature range. Question marks may indicate doubt concerning proper classification of the observed change, the reality of any change at that temperature, or the correctness of the temperature reported for the observed change. In addition to the transitions reported in the table, the 58.8 per cent and 57.2 per cent samples underwent a change at 50° and 63°C., respectively, to a coarse mottled structure, similar to that of middle soap at low temperatures.

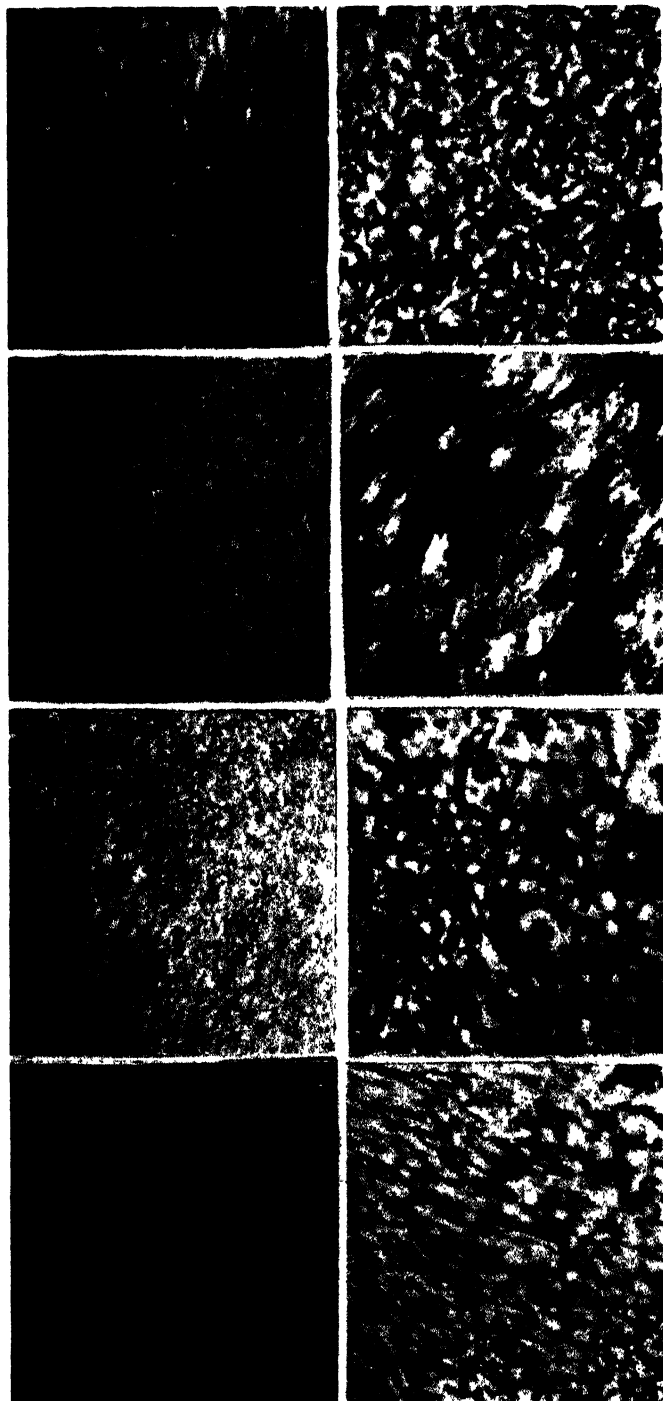


FIG. 1. Anhydrous sodium oleate (IV) at 89°C

FIG. 2. Anhydrous sodium oleate (III) at 153°C

FIG. 3. Anhydrous sodium oleate (I) at 220°C.

FIG. 4. 89 per cent sodium oleate (A) at 220°C.

FIG. 5. 67 per cent sodium oleate (A) at 216°C.

FIG. 6. 89 per cent sodium oleate (B) at 144°C

FIG. 7. 67 per cent sodium oleate, at 84°C.

FIG. 8. Appearance of middle soap at lower temperatures, 36.3 per cent sodium oleate at 80°C.

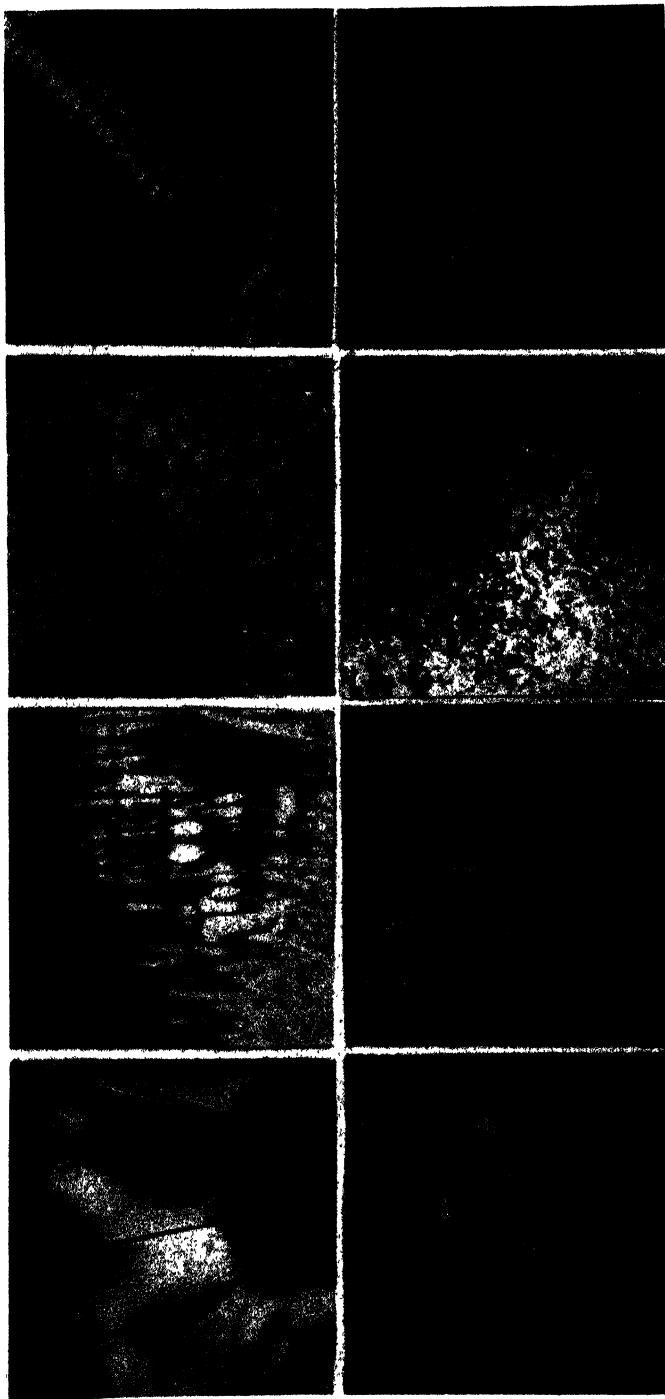


FIG. 9. Focal conic structures in middle soap, 36.3 per cent sodium oleate at 115°C.

FIG. 10. "Palisade structure"; 89 per cent sodium oleate at 222°C.

FIG. 11. Neat soap in equilibrium with isotropic liquid; 58.8 per cent sodium oleate at 90°C.

FIG. 12. "Oily streaks" (olige Streifen) at the meniscus of a bubble in the isotropic liquid, 90.3 per cent sodium oleate at 235°C.

FIG. 13. Inverted focal conic structures in isotropic liquid, 90.3 per cent sodium oleate at 235°C.

FIG. 14. Batonnets in isotropic liquid; 52.8 per cent sodium oleate at 189°C.

FIG. 15. Change in microscopic appearance described in column 6 of table 3; 89 per cent sodium oleate at 98°C.

FIG. 16. 58.8 per cent sodium oleate at 48°C.

basis of other evidence. Waxy soap (phase III) (see figure 2) has not yet been distinguished microscopically from superwaxy soap (phase II) in this system, despite the dilatometrically established transition temperature between the two at 179°C.

Characteristic optical forms, some of which develop when the system is held at constant temperature for an hour or so and some of which appear immediately on formation of liquid crystal from isotropic liquid, are shown in figures 9 to 14.

Despite its limitations, the microscopic method has proved very useful. In some instances the characteristic appearances have served to distinguish one phase from another, thus supporting the hypothesis of their separate existence, even though they are not adequate to fix the boundaries quantitatively. However, it is the general conclusions from the totality of the data that are significant, rather than the individual observations.

Phase separation

The mechanical separation of the phases coexisting at equilibrium in soap systems and analysis of the two layers is usually impossible, because the high viscosity of the phases and the small differences in their density make spontaneous separation, if any, slow and incomplete. One exception to this common experience is the equilibrium involving phase B and isotropic liquid. On standing 24 hr. in an air oven at constant temperature, systems in this range of composition separate into an upper liquid crystalline layer and a lower isotropic layer. The compositions of the two layers can be calculated from their relative volumes (measured by their relative heights in a cylindrical tube) in any pair of systems at the same temperature by means of the usual tie-line relation. This procedure was employed with five to eight tubes at nine temperatures; the results are shown in table 4.

In addition, seventeen tubes varying in composition from 25.0 to 96.0 per cent sodium oleate were hung in a viewing thermostat and observed at 54°, 64°, 74°, 85°, and 95°C. They were then examined in air between crossed Polaroids, and up-ended and tapped to observe flow properties. In general the appearance of these systems was in accord with the presumed phase relations deduced from the preceding data. For example, at 74°C. a series of tubes arranged in order of increasing soap concentration were found to have the following appearance: (1) mobile, light yellow, transparent, isotropic liquid; (2) stiff mixture of practically transparent anisotropic middle soap and isotropic liquid; (3) homogeneous, transparent, anisotropic middle soap which barely flowed; (4) mixture of middle soap and isotropic liquid, which flowed stiffly; (5) two-layer systems with a sharp interface, consisting of rather transparent anisotropic material on top (like settled neat soap) and isotropic liquid on the bottom, flowing

easily; (6) milky yellow, anisotropic, plastic material (soap boiler's neat soap) which flowed stiffly but fairly easily; (7) heterogeneous mixture of this neat soap and opaque, white, waxy or crystalline material, either rigid or barely flowing; and (8) nearly white, opaque, solid material. In order to harmonize the observations with the suggested phase rule diagram it is necessary to assume that the milky yellow material noted under (6) and the clearer, anisotropic material noted under (5) do not differ in a phase rule sense.

According to the diagram, as soap concentration is increased at 74°C. the system should go through the following phase changes: (1) isotropic liquid to 28 per cent; (2) middle soap and isotropic liquid from 28 to 30.7 per cent; (3) middle soap between 30.7 and 41.7 per cent; (4) middle soap and isotropic liquid from 41.7 to 43.4 per cent; (5) isotropic liquid between 43.4 and 43.7 per cent; (6) isotropic liquid and neat soap between 43.7 and 69.5 per cent; (7) neat soap between 69.5 and 79.8 per cent; (8) neat soap and waxy soap from 79.8 to 84.6 per cent; (9) waxy soap between 84.6 and 85.5 per cent; (10) waxy soap and subwaxy soap from 85.5 to 90.4 per cent; and (11) subwaxy soap between 90.4 and 100 per cent.

EXPERIMENTAL RESULTS

A possible phase rule diagram (figure 17) can be suggested on the basis of the preceding data.

The boundary of the field of isotropic solutions is uniquely and accurately determined by the T_i data (table 1), together with that portion of the T_c data referring to formation of isotropic liquid on heating. Experiments with another supply of sodium oleate (Merek) gave a T_i curve qualitatively similar to that shown but differing from it by about 10°C.

The boundaries outlining the field of existence of middle soap are reasonably well established by the T_c curve, by the three observations of T_0 shown in the figure, and by the fact that the middle soap boundary must touch the T_i curve at its maximum point with a horizontal tangent. The T_c curve at the bottom of the middle soap region is so flat that its exact course can not be determined from the experimental points. It was drawn as shown by analogy with the behavior of other soap systems.

The temperature (70°C.) at which neat soap, middle soap, and isotropic liquid are all in equilibrium is determined by the three T_0 observations shown in the diagram and by the fact that below this temperature both the phases in two-layer systems were anisotropic between crossed Polaroids. However, there is some microscopic evidence tending to show that possibly isotropic liquid may be present at temperatures down to nearly 60°C.

The evidence that phases A and B may be isolated and have no counterpart in anhydrous soap lies principally in the great difference in the microscopic appearance of the samples. Within the boundaries of phase B

as drawn, samples have the type of appearance shown in figure 6, while more concentrated systems do not show marked differences from the appearance of the anhydrous soap phases shown in figures 1 to 3. Moreover, samples containing more than 90 per cent sodium oleate show a large number of changes as the temperature is raised, whereas samples containing between 80 and 90 per cent soap show little change over a wide temperature interval within the area assigned on the diagram to phase B.

The lower boundaries of phase B are indicated by T_c , vapor pressure data, and phase separation data, together with visual and microscopic observations. Some uncertainty is introduced by the fact that in addition to the T_c points defining the curve, rather reproducible observations were

TABLE 4*
Visual observation of separation of phases

NUMBER OF SYSTEMS USED	TEMPERATURE	COMPOSITION, WEIGHT PER CENT NaOl	
		Liquid crystal	Isotropic liquid
	°C.		
4	146	60.7 \pm 2.0	48.1 \pm 1.6
4	137	63.6 \pm 1.0	45.4 \pm 1.1
5	127	66.7 \pm 1.8	43.2 \pm 2.0
7	112	67.4 \pm 0.6	46.5 \pm 0.4
5	107	70.0 \pm 3.1	44.7 \pm 1.7
5	99	68.8 \pm 1.4	44.5 \pm 0.8
5	89	69.5 \pm 1.0	42.6 \pm 2.3
6	82	69.7 \pm 1.5	41.7 \pm 1.6
6	71	69.1 \pm 0.8	40.1 \pm 1.1

* Values at 89°, 82°, and 71°C. were obtained after the sealed glass tubes had been left at room temperature over the summer following storage at temperatures between 70° and 160°C. for about a month. This may account for the apparent abrupt shift in the value of the composition of the isotropic liquid at these temperatures.

also made of a set of temperatures at which the soap system became considerably more translucent. The course of the curve defined by these observations is indicated in figure 17 by the black dots crossing the neat soap region at 80°C., according to the values placed in parentheses in table 1. Although this is a perfectly real change in appearance it is our present presumption that it does not denote any change of phase, but this conclusion still needs confirmation by more objective experimental evidence.

The reality of the upper boundary of soap boiler's neat soap (phase B) is still indefinite. Its upper temperature limit, at which phases A and B and isotropic liquid coexist, seems defined by the flat in the T_c curve at 224°C. and 91.5 to 94.4 per cent sodium oleate. The T_c curve and the

curve defined by phase separation data, extrapolated, seem to indicate a similar break at 165°C. between 55 and 58.5 per cent soap. Also, the T_c curve may have a slight inflection near 165°C. In this region of composition and temperature, liquid crystal was observed to form from isotropic liquid *on heating*, as would be expected from the diagram as drawn. Finally, in the region represented as containing the two phases A and B, the apparent viscosity goes through a minimum, as might be expected of a heterogeneous mixture. Microscopically, phases A and B display certain characteristic differences as shown in figures 4, 5, and 6. On the basis of all these indications the lower boundary of phase A and the upper boundary of phase B are dotted in as shown.

The name "phase A" is only a tentative designation and should be replaced by a more satisfactory terminology such as "superneat soap," if its separate existence is confirmed. Historically, "neat soap" (phase B) is always used for the soap layer present in the kettle during the fitting and settling process (*ca.* 69 per cent soap, *ca.* 100°C.). A discontinuity is here indicated between the neat soap of the soap boiler and the anhydrous phases. The phase which may be called "anhydrous neat soap" does not appear to exist for pure sodium oleate (M. J. Vold and M. Macomber, unpublished work).

The transition temperatures between the different phases of anhydrous sodium oleate at higher temperatures are fairly well established from the dilatometric data. The positions of the boundaries of these same phases in the aqueous systems are inferred largely from microscopic observations, confirmed in some instances by dilatometric points. The positions of the various invariant temperatures marking the coexistence of three condensed phases are suggested partly by flats and inflections in the T_c curve and partly by changes in microscopic appearance or inflections in dilatometer curves.

DISCUSSION

Applicability of the phase rule

The colloidal state is sometimes regarded as "autonomous," and it is assumed that the classical laws of physical chemistry, as, for example, the phase rule, are of only limited validity in such systems (2). However, McBain (12) and McBain and McBain (12a) have demonstrated true reversible equilibria between colloidal sols and molecular solutions as well as crystals, and McBain, Vold, and Vold (13), in discussing the application of the phase rule to soap systems, concluded that it must apply directly in its classical form, since, when time is allowed for the realization of true equilibrium, the state of a soap system is governed solely by temperature, pressure, and composition. The applicability of the phase rule is governed not by whether or not the system is classified as colloidal but by

whether there is established a final equilibrium that depends only on temperature, pressure, and composition, independent of the process by which these variables are brought to their final values.

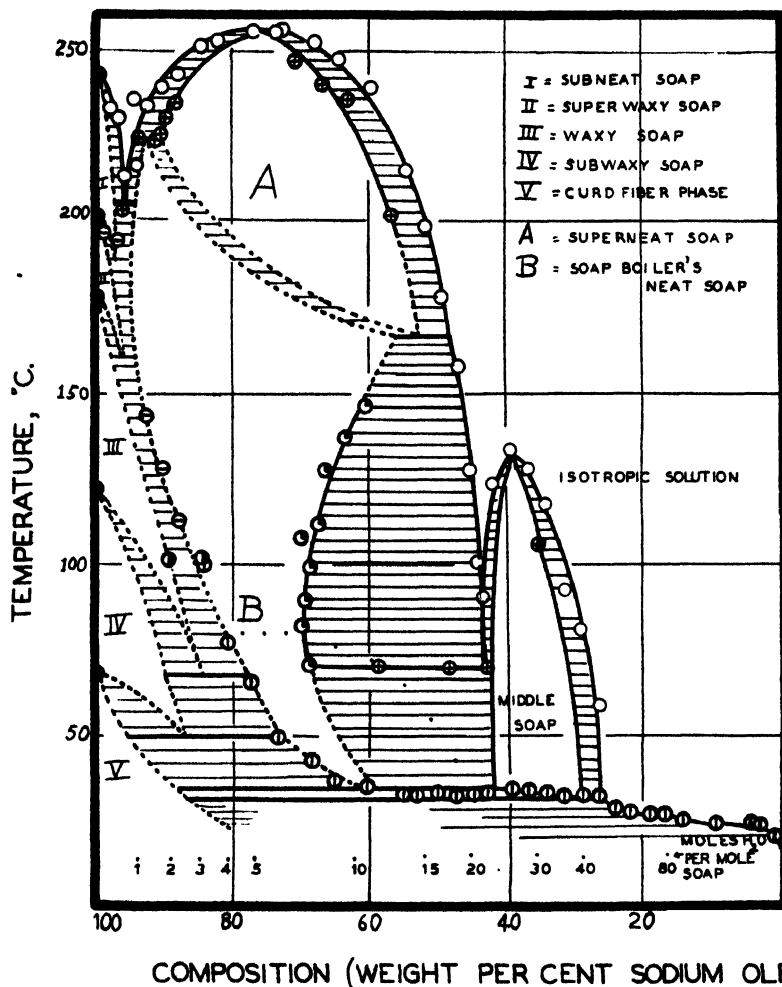


FIG. 17. Phase rule diagram of the system sodium oleate-water. \circ , T_i ; \oplus , T_0 ; \bullet , dilatometric results; \odot , vapor pressure results; \ominus , T_a ; \ominus , " T_c " obtained on cooling; \ominus , data from phase separation; \bullet , small black dots representing changes in visual appearance of doubtful phase significance.

The diagram itself (figure 17), which is an expression of the realization of these conditions, is the most convincing demonstration of the applicability of the phase rule to these soap systems. The existence of quasi-crystalline particles in clear, transparent, isotropic, non-hydrolyzed soap

solutions has recently been demonstrated by means of x-rays (3). Specific instances of conformity to the predictions of the phase rule in equilibria in which this colloidal isotropic liquid is one of the participating phases may be pointed out. For example, the temperature of disappearance of curd fiber phase is independent of composition over the composition range where both middle soap and isotropic liquid are formed in the process, i.e., $F = c + 1 - p$ for a condensed system, $= 2 + 1 - 3 = 0$, where three phases are simultaneously present. Identical results were obtained for the portion of the T_c curve involving melting to isotropic liquid by both heating and cooling, and it was shown that values obtained after 3 months checked exactly those obtained with freshly prepared samples. A similar independence of aging was noted by McBain and collaborators in the case of the sodium palmitate system (10, 11). Again, despite the relatively large experimental error of the method, the data of table 4 show that the usual tie-line law is obeyed.

Undercooling

Although equilibrium can be realized, soap systems may often persist for considerable lengths of time in an unstable state. Sodium oleate middle soap, undercooled with respect to formation of curd phase, often lasted several days and required months for complete curding even after the process was initiated. Curd fibers possibly require years to reach a final equilibrium (4, 14). In general, sodium oleate systems appear to undergo various phase changes much more slowly than do the saturated soaps. Some of the difficulties experienced by Smith (15) in his experiments with sodium oleate extending over only a few hours may be ascribable to this fact.

It has been a matter of common experience (8, 10, 11) that undercooling does not occur with respect to formation of liquid crystal from isotropic liquid, this fact having a theoretical foundation by analogy with the deduction from kinetic theory (10) that undercooling can not occur with respect to formation of two liquid phases. This same generalization also applies to the sodium oleate system, except that in one case, that of a 36.3 per cent soap system, the isotropic liquid was undercooled from 130°C. to room temperature, as was evident from its appearance in the microscope between crossed Nicols, and formed middle soap only on subsequent heating. This phenomenon is doubtless due to the existence of a fairly high degree of molecular order in middle soap. Again, while T_c was perfectly reproducible in systems forming phase A from isotropic liquid, thereby proving that no inhomogeneities of composition had developed during study of the sample, the complete disappearance of the isotropic liquid was often very slow, sometimes not being complete until as much as 50°C. below the temperature at which isotropic liquid first appeared on heating.

Orientation at surfaces, etc.

At the edges of bubbles, or in thin layers in contact with glass, the liquid crystalline phases may be highly oriented and may sometimes persist to temperatures as much as 7°C. higher than in the bulk of the soap. This effect may be analogous to the transmission of surface forces over macroscopically observable distances through an adhesive film so that the breaking strength of the adhesive itself is determined by the materials that it joins (9). This behavior at the surface is not described by the usual form of the phase rule, but it is a phenomenon occurring only at the surface of the bulk phase, and so does not affect the application of the phase rule to the bulk of the system.

In one case (96.5 per cent sodium oleate)—for three independent microscopic samples—dull anisotropic patches were present in the isotropic liquid at variable temperatures 8°C. to 45°C. above T_i (200°C.). Although these clusters formed repeatedly in this system, they could not be confused with the reproducible formation and disappearance of bright liquid crystal at T_i . Possibly they are oriented groups of molecules analogous to tactoids and probably do not constitute a separate phase.

Nature of the liquid crystalline phases

The succession of phase changes in anhydrous sodium oleate as the temperature is raised seems to be the same as that already reported for anhydrous sodium palmitate, the only difference being that sodium oleate apparently has one less transition (18). It is reasonable to assume that the difference from one to another is in the degree of regularity of arrangement, rather than solely in crystal form or its liquid crystal equivalent. The idea has been advanced (18) that the large number of transitions constitute a stepwise disintegration of the soap lattice, resulting from very great differences between the strength of the crystal forces in different directions.

These anhydrous phases do not appear to be capable of dissolving much water without losing their identity. In general, addition of even small amounts of water lowers any given transition temperature significantly, corresponding to a marked weakening of the residual crystal forces responsible for the stability of the phase. When the water content exceeds a maximum value of 3 moles of water per mole of soap, the succession of homogeneous phases is no longer observed, but instead a smaller number of liquid crystalline phases capable of containing much larger amounts of water seem to be formed.

Published diagrams for other soaps (7, 11) do not show the maximum in the T_i curve denoting the presence of phase A. As yet unpublished experiments of Miss Mary Frick in this laboratory show, however, that it does exist for sodium stearate, sodium palmitate, and probably for sodium

laurate, and is therefore not a peculiarity of the unsaturated soap, sodium oleate.

The characteristic optical forms shown in figures 9 to 14 are all recognized² (1) as characteristic of the smectic type of liquid crystal. However, the large focal conic structure shown in figure 9 has been found only in middle soap, and has not been observed with superneat or neat soap. Again, middle soap has not been observed in the form of batonnets, an orientation very common to superneat and neat soap as well as to the subneat phase of anhydrous soap. Small, round, curiously marked and bounded figures, one of which is visible in the lower left center of figure 11, are formed with neat soap in equilibrium with isotropic liquid or middle soap at temperatures below 100°C. Consequently, although all these phases seem to be of the smectic type, there may be some structural differences between them.

SUMMARY

A partial study of the phase rule behavior of the system sodium oleate-water has been carried out using many independent methods, including visual observation of the temperatures of phase change, dilatometric experiments, isothermal vapor pressure determinations, phase separations, and microscopic examination between crossed Nicols. It has been found that a much larger number of separate phases exist than had previously been recognized in systems of soap and water, although the data are not yet sufficient to define all the phase boundaries.

All the equilibria, in so far as these have been determined, and including those in which the participating phases are colloidal in nature, have been successfully represented on a phase rule diagram in which the sole independent variables are temperature and composition.

The successive phases of anhydrous or nearly anhydrous sodium oleate occurring with rising temperature may represent stepwise disintegration of the crystalline lattice, each phase being less regular than its predecessor. The separate aqueous liquid crystalline or anisotropic liquid phases, which may have no anhydrous counterparts, are all smectic in type, as shown by their characteristic optical properties.

The author wishes to express his appreciation to Professor J. W. McBain for many valuable discussions during the course of this investigation.

REFERENCES

- (1) FRIEDEL, G.: Chapter 3 in Alexander's Colloid Chemistry, Vol. I. The Chemical Catalog Co., Inc., New York (1926). LAWRENCE, A. S. C.: J. Roy. Microscop. Soc. 58, 30 (1938).

² The author is also indebted to J. D. Bernal for assistance in recognizing some of these forms.

- (2) HAUSER, E. A.: Colloidal Phenomena, p. 55. McGraw-Hill Book Co., New York (1939).
- (3) HESS, K., AND GUNDERMANN, J.: Ber. **70B**, 1800 (1937). HESS, K., PHILIPPOFF, W., AND KIESSIG, H.: Kolloid-Z. **88**, 40 (1939).
- (4) LAING, M. E., AND MCBAIN, J. W.: J. Chem. Soc. **117**, 1506 (1920).
- (5) MCBAIN, J. W.: Nature **114**, 49 (1924).
- (6) MCBAIN, J. W., AND BAKER, A. M.: J. Am. Chem. Soc. **48**, 690 (1926).
- (7) MCBAIN, J. W., BROCK, G. C., VOLD, R. D., AND VOLD, M. J.: J. Am. Chem. Soc. **60**, 1870 (1938).
- (8) MCBAIN, J. W., AND ELFORD, W. J.: J. Chem. Soc. **1926**, 421.
- (9) MCBAIN, J. W., AND FULLER, G. W.: Unpublished data.
- (10) MCBAIN, J. W., AND LANGDON, G. M.: J. Chem. Soc. **127**, 852 (1925).
- (11) MCBAIN, J. W., LAZARUS, L. H., AND PITZER, A. V.: Z. physik. Chem. **A147**, 87 (1930).
- (12) MCBAIN, J. W.: Kolloid-Z. **40**, 1 (1926).
- (12a) MCBAIN, J. W., AND MCBAIN, M. E. L.: J. Am. Chem. Soc. **58**, 2610 (1936).
See also MCBAIN, J. W., AND WOO, T. M.: J. Am. Chem. Soc. **60**, 223 (1938); J. Phys. Chem. **42**, 1099 (1938); Kolloid-Z. **87**, 74 (1939).
- (13) MCBAIN, J. W., VOLD, R. D., AND VOLD, M. J.: J. Am. Chem. Soc. **60**, 1866 (1938).
- (14) MCBAIN, J. W., WORDEN, M., AND MCDOWELL, J. M.: J. Am. Chem. Soc. **61**, 2540 (1939).
- (15) SMITH, E. L.: J. Phys. Chem. **36**, 2455 (1932).
- (16) VOLD, R. D., AND FERGUSON, R. H.: J. Am. Chem. Soc. **60**, 2066 (1938).
- (17) VOLD, R. D., ROSEVEAR, F. B., AND FERGUSON, R. H.: Oil & Soap **16**, 48 (1939).
- (18) VOLD, R. D., AND VOLD, M. J.: J. Am. Chem. Soc. **61**, 808 (1939).

NEW BOOKS

A Manual of Radioactivity. By GEORGE HEVESY AND FRITZ PANETH. Translated by R. W. LAWSON. Second English edition. xvi + 306 pp. Oxford: University Press, 1938. Price: \$5.50.

This is the second English edition of the well-known textbook on radioactivity. It is not a translation of the second German edition (1931) but is a complete and a thorough revision of the subject matter up to date. The authors are well known for their researches in radioactivity and particularly in the field of radioactive indicators, which they have introduced in the investigations of problems in physics, chemistry, and biology. The book is excellent for the amount of material chosen for a textbook, the subject matter itself, and the presentation of the science of radioactivity and the artificial disintegration of atoms.

The textbook is divided into twenty-six chapters. The introductory chapter deals with the disintegration theory of radioactive atoms, the phenomena observed as a result of the action of the emitted radiation on matter through which it passes, and the utilization of these effects in the study of what is happening to the radioactive atoms. The electrical method of study, including also the Geiger counter, is particularly stressed. The following five chapters deal with the radiations known as alpha, beta, gamma, secondary, and recoil rays. Under the heading of secondary radiation, characteristic x-rays are dealt with in some detail. The processes of ionization are also clearly pointed out, where charged particles produce the effect as well as where a quantum of energy is involved. The nature of the rays, as well as the effects produced by them, are considered in sufficient detail. Positrons and neutrons receive adequate consideration in chapter VII.

Chapter VIII, entitled "Constitution of the Atom and Radioactive Rays", seems to be improperly labelled. It considers Bohr's theory and admirably presents its elements and a picture of the electronic structure. Simple mathematical (appendix) discussion is given and reference is also made to de Broglie's wave theory of matter and Schrödinger's equation.

Chapter IX deals with the nucleus. It gives the historical development of the idea of the nuclear atom, the conception of isotopes, the potential barriers existing to the penetration of charged particles in either direction, the nuclear energy levels, and the emission of alpha, beta, and gamma rays.

The next five chapters are devoted to the study of the transmutation of elements, whether they are natural or artificially radioactive substances. The theory of disintegration is developed from the mathematical point of view, and formulas are deduced (a) for cases of radioactive series starting with the parent substance alone and (b) for the case of initial radioactive equilibrium. Considerable space is devoted to the three natural series and to the discussion of the half-value period in its relation to the energy of disintegration of the atom.

Chapters XV to XVII deal with the chemical properties of natural radioactive substances, their position in the periodic table, bringing out the displacement law for alpha or beta emissions, and with isotopes. Chapter XVIII continues the discussion of radioactive isotopes as radioactive indicators in application to problems in physics, chemistry, and biology, in which field the authors have made the initial and greatest contributions themselves.

Methods of studying non-radioactive isotopes by various physical means and modes of their separation are given briefly in the following three chapters.

The remaining chapters (five) are devoted to the consideration of the preparation of radioactive substances, the chemical properties of individual radioelements, various effects of the radiations, problems of the age of minerals, and cosmic rays. A short appendix describes the cyclotron. The text is supplemented with fifty-seven tables and fifty-four figures.

The book should prove to be an excellent text for honor students in the natural sciences.

ALOIS F. KOVARIK.

A Treatise on Light. By R. A. HOUSTOUN. 22 x 14 cm: xi + 528 pp.; 8 plates. London: Longmans, Green and Company, 1938. Price: 14/-.

This new edition of Dr. Houstoun's standard treatise shows signs of a thorough revision, and new matter has been incorporated in places to amplify the older work.

A new chapter, forming a good general introduction to the quantum theory, has also been added, but the general plan of the book remains unaltered. This has much to recommend it.

The whole work is divided superficially into four parts but essentially into two, the first of which, in three sections, covers geometrical optics, physical optics, spectroscopy, and photometry. The remaining part, entitled "Mathematical Theory", supplements more particularly the sections on physical optics and spectroscopy. This arrangement enables due emphasis to fall upon the physical concepts involved, so that a proper balance is maintained between the different aspects of the subject.

The newer applications of optical instruments receive consideration in this edition, but it is to be hoped that a later edition would allow space for a more extended treatment, for example, of x-ray analysis, colorimetry, turbidimetry, and the Raman effect. The rapid strides made by the theory of spectra in recent years have had a revolutionary effect upon theories of the structure of matter and have placed a very valuable tool in the hands of the investigator. It is therefore rather disappointing to find that Dr. Houstoun should abandon this child upon the doorstep of "mathematical chemistry". The student will, moreover, find no references to facilitate an introduction to this field. Throughout the work, indeed, the lack, in all but a few cases, of references to original works is to be considered a shortcoming.

From other points of view this edition is well adapted to the use of students. The book is well got up, the exposition is clear, and the style is easy. A number of plates and the answers to the exercises have been added. The present edition gives the impression of a well-considered and, on the whole, an accurate and reliable work.

J. W. PERRY.

Kurze Geschichte der Katalyse in Praxis und Theorie. By A. MITTASCH. 22 x 14 cm.; viii + 139 pp. Berlin: J. Springer, 1939. Price: 6.60 RM.

In this small book a historical survey of the development of the study of catalysis up to the present day is combined with a concise yet informative presentation of the main facts and theories of catalytic phenomena. All the important stages of development are reviewed, and the contributions of the numerous workers are clearly stated. The author emphasizes the leading part played by Ostwald in reviving and extending studies in this field, and he continues the story to the present stage of investigation. The book is one that every chemist will read with pleasure.

J. R. PARTINGTON.

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